Talanta 201 (2019) 413–418

Contents lists available at ScienceDirect

Talanta

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

Covalent immobilization of covalent organic framework on stainless steel wire for solid-phase microextraction GC-MS/MS determination of sixteen polycyclic aromatic hydrocarbons in grilled meat samples

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ARTICLE INFO

Keywords:
Solid-phase microextraction
Covalent organic frameworks
Polycyclic aromatic hydrocarbons
GC-MS
Grilled meat

ABSTRACT

Covalent organic framework TpBD was grafted on stainless steel wire with polydopamine as a linker. The fabricated TpBD bonded stainless steel wire was used as the solid-phase microextraction fiber to extract sixteen polycyclic aromatic hydrocarbons (PAHs) for subsequent GC-MS/MS determination in grilled meat samples. The developed method gave the limits of detection ($S/N = 3$) from 0.02 (pyrene)-1.66 (naphthalene) ng L^{-1} and enhancement factors from 1069 (naphthalene)-10879 (benz(a)anthracene). The relative standard deviations (RSDs) for intra-day and inter-day study are in the range of 2.6%–8.5% and 4.5%–9.4%, respectively. The fiber-to-fiber RSDs for three parallel prepared fibers were 5.3%–10.0%. One TpBD bonded fiber can stand at least 200 cycles without significant loss of extraction efficiency. The developed method was successfully applied for the determination of trace PAHs in grilled meat samples with recoveries from 85.1% to 102.8%.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), as a class of teratogenic, carcinogenic, persistent compounds, contaminate food through environmental sources (e.g., adsorption by plants from polluted groundwater, intake by seafood in contaminated zones) or food preparation (e.g., grilling, roasting, or smoking) [1–3]. Sixteen PAHs (naphthalene (NaP), acenaphthylene (AcPY), acenaphthene (AcP), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbFL), benzo(k)fluoranthene (BkFL), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (InP), dibenz(a,h)anthracene (DBA) and benzo(g,h,i)perylene (BghiP)) were defined as priority pollutants by the Environmental Protection Agency (EPA) due to their toxicity and potential for human exposure [4]. The allowable maximum residue level (MRL) of BaP is under 0.2 μg L^{-1} for bottled water in the United States [5]. The tolerant maximum level of BaP and the amount of PAH4 (containing BaP, BaA, BbFL and Chr) in grilled meat set by the European Food Safety Authority are 2 and 12 μg kg^{-1}, respectively [6]. However, the determination of PAHs is difficult owing to the low concentration in complex food samples. Therefore, developing a method for enrichment and detection of trace PAHs in food is of great importance.

Solid-phase microextraction (SPME), as a solvent-free extraction technique, has been used widely for sample pretreatment owing to its characteristics of integrating sampling, extraction and sampling introduction in one step [7–9]. The structure and properties of the coating play an important role in SPME. Various types of commercial SPME coatings are available, such as polyacrylate (PA) [10], poly(dimethylsiloxane) (PDMS) [11,12], and poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) [13,14]. However, their performance is not always satisfactory due to the drawbacks such as short lifetime, insufficient thermal or solvent instability, limited selectivity and fragile matrix. Hence, the preparation of durable and efficient coating of SPME is necessary.

Covalent organic frameworks (COFs), featured by large area surface, good chemical stability, remarkable thermal stability and modifiable pores [15–19], have been studied widely in many fields, such as adsorption [20], gas storage [21], extraction [22–24], catalysis [25–27], separation [28,29] and sensing [30]. The aromatic functionalities and tunable pore size structures make COFs potential as outstanding coating

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https://doi.org/10.1016/j.talanta.2019.04.031
Received 4 March 2019; Received in revised form 9 April 2019; Accepted 11 April 2019

materials of SPME [31–33], especially for the analysis of aromatic compounds [34].

Herein, we report the use of polydopamine (PDA) as a linker for covalent bonding of COF TpBD onto stainless steel wire as an efficient and durable SPME fiber. The prepared fiber is then used to develop a SPME method for gas chromatography-tandem mass spectrometry (GC-MS/MS) determination of 16 trace PAHs. The developed method is applied for the determination of trace 16 PAHs in different grilled meat samples including mutton shashlik, grilled bacon and grilled chicken wings with quantitative recovery, wide linearity, excellent reproducibility and large enhancement factors (EFs).

2. Experimental section

2.1. Chemicals and materials

All reagents used were at least of analytical grade, if not otherwise described. Ultrapure water was obtained from Wahaha Foods Co., Ltd. (Hangzhou, China). 1,3,5-Triformylphloroglucinol (Tp) was obtained from Chengdu Tongchuangyuan Pharmaceutical Technology Co. (Chengdu, China). Benzidine (BD) and mesitylene were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Dioxane, acetone, methyl alcohol, N, N-dimethylformamide, tetrahydrofuran, hydrochloric acid, nitric acid and glacial acetic acid were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Dopamine (DA) was obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). Chromatographic grade acetonitrile was bought from Thermo Fisher (Shanghai, China). The stainless steel wire (SSW) and 5 μL gas chromatograph microsyringes were purchased from Shanghai High Pigeon Industry and Trade Co., Ltd. (Shanghai, China). The mixture standard solution of 16 PAHs in acetonitrile (200 mg L^{-1} each) was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). The stock solution of the PAHs at 20 mg L^{-1} was prepared in acetonitrile and stored at −20 °C. 100 μg L^{-1} of the mixture standard solution of the PAHs was obtained by step-by-step dilution of the stock solution with acetonitrile. Working standard solutions of the PAHs were prepared by diluting 100 μg L^{-1} acetonitrile solution of PAHs with ultrapure water.

2.2. Instrumentation

The morphology of the coating was characterized on a su1510 scanning electron microscope (SEM, HITACHI, Japan). Thermogravimetric analysis (TGA) was performed on a Q500 TG instrument (TA, USA) from 50 °C to 800 °C in flowing N_2 at a heating rate of 10 °C min^{-1}. The X-ray diffraction spectrometry (XRD) patterns were recorded on a D2 PHASER (BRUKER AXS GMBH, Germany). Fourier transform-infrared (FT-IR) spectra were obtained on an IS10 FT-IR spectrophotometer (Nicolet, USA). The 30 μm PDMS commercial SPME was obtained from Supelco (Bellefonte, USA). A Bear QSJ-B03H2 blender was used to deal with meat samples (Foushan, China).

2.3. GC-MS/MS and operating condition

A gas chromatograph (GC) system (7890B, Agilent, USA) coupled with a triple quadrupole mass spectrometer (7000D, Agilent, USA) was used for separation and quantification. The column used for separation was Rxi-5MS (30 m × 0.25 mm × 0.25 μm) (Shimadzu, Japan). The high purity helium was employed as carrier gas at a flow rate of 1.0 mL min^{-1}. The injector was operated in the pulsed splitless mode, injection pulse pressure: 25 psi until 0.9 min; purge flow to split vent: 50 mL min^{-1} at 4 min; injector temperature, 300 °C. The oven temperature program was as follows: initial oven temperature, 80 °C, 25 °C min^{-1} to 180 °C, 10 °C min^{-1} to 220 °C, 5 °C min^{-1} to 240 °C (held for 4 min), 2 °C min^{-1} to 260 °C (held for 2 min), 17 °C min^{-1} to 310 °C (held for 3 min). The mass spectrometer parameters were as follows: interface temperature, 300 °C; source temperature, 320 °C; energy of electron, 70 eV. The mass spectrometer was operated in the electron ionization (EI) mode with quadrupole temperature of 150 °C. Analysis was performed in multi-reaction monitoring (MRM) mode. Other parameters for the determination of 16 PAHs are shown in Table S1.

2.4. Fabrication of the TpBD bonded SPME fiber

The TpBD was prepared according to Li et al. [35]. The TpBD bonded fiber was fabricated as follows: the end (3 cm) of a 17-cm stainless steel wire was etched with aqua regia for 30 min to obtain rough surface, washed with ultrapure water and dried in air. The etched fiber was then immersed into the DA solution (50 mg DA, 25 mL Tris-HCl buffer solution (pH 8.5)) with stirring at 35 °C for 12 h. The resulting PDA modified fiber was gently washed with ultrapure water, and dried in oven (80 °C) for 12 h. The dried PDA modified fiber was immersed in the solution of Tris-HCl (4 mL, pH 8.5) containing BD (83 mg) in a 30 mL Teflon-lined stainless steel bomb in a vacuum oven (80 °C) for 4 h to graft BD on PDA modified fiber for subsequent TpBD growth. The BD grafted PDA-modified fiber was dried in oven at room temperature, and then immersed into a mixture of Tp (63 mg), BD (83 mg), mesitylene (4 mL), dioxane (4 mL) and acetic acid (9 mol L^{-1}, 0.5 mL) in the Teflon-lined stainless steel bomb in vacuum oven at 120 °C for 48 h to obtain TpBD bonded fiber. Finally, the TpBD bonded fiber was immersed in acetone for 3 days to remove residual ligands and dried in an oven at room temperature. In this way, the TpBD bonded SPME fiber was obtained.

2.5. Collection and pretreatment of real samples

The grilled meat samples were collected from local supermarkets, and homogenized with a blender. 2.0 g of the homogenized meat was mixed with 10 mL of acetonitrile in a 50 mL centrifuge tube. The mixture was ultrasonicated for 20 min to extract the PAHs, and centrifuged at 10000 rpm for 10 min to collect the supernatant. The residual meat was extracted with another 10 mL of acetonitrile to obtain the second supernatant in the same way. The total collected supernatant (ca. 20 mL) was concentrated to dryness with flowing N_2. The residues were dissolved in 1 mL acetonitrile and diluted 1000 times with ultrapure water for SPME experiments.

2.6. SPME procedures

The prepared TpBD bonded SPME fiber was conditioned at GC injection port at 310 °C until the baseline was stable before extraction. The conditioned TpBD bonded fiber was immersed into the standard solution or the sample solution in a sample vial at 40 °C for 50 min SPME under stirring (600 rpm). The TpBD bonded fiber was then removed from the vial and inserted into the GC inlet for GC-MS/MS analysis.

3. Results and discussion

3.1. Fabrication and characterization of the TpBD bonded SPME fiber

Fig. 1 shows a schematic fabrication of TpBD bonded SPME fiber. Aqua regia etching of the bare stainless steel wire led to the rough surface of the stainless steel wire (Fig. 2A and B). PDA was introduced to chelate the metal ions on the rough surface of the etched stainless steel wire to provide functional group for further modification. The successful PDA modification was evidenced from the formation of uniform particles on the surface of stainless steel wire (Fig. 2C and D), and the presence of the PDA characteristic peaks at 3500-3100 cm^{-1} for the O-H of the phenolic hydroxyl group and the N-H of amino and imino group and 1604 cm^{-1} for the C=C of benzene ring, and

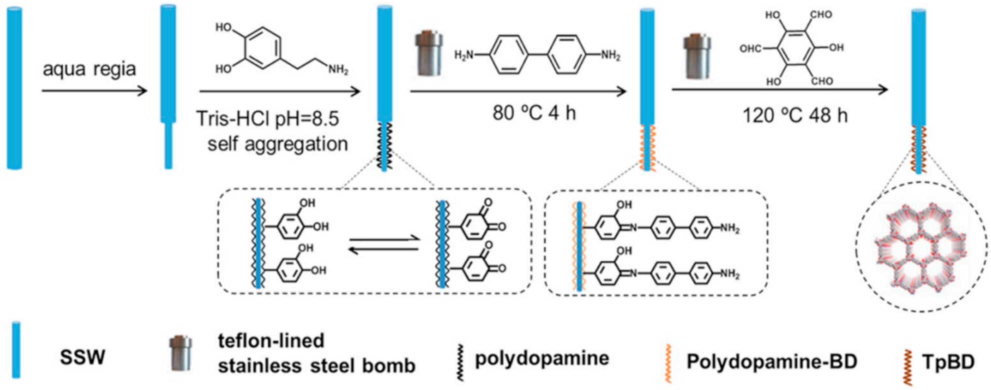

Fig. 1. Schematic illustration for fabricating the TpBD bonded SPME fiber.

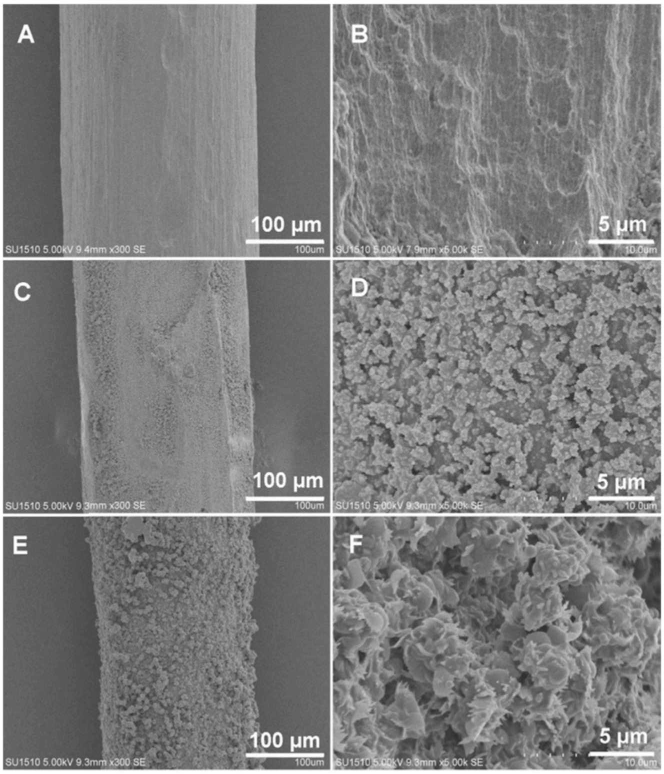

Fig. 2. SEM images of the etched fiber (magnifications of A 300 × , B 5000 ×), the PDA coated SPME fiber (magnifications of C 300 × , D 5000 ×) and the TpBD bonded SPME fiber (magnifications of E 300 × , F 5000 ×).

1512 cm^{-1} for the N-H in FT-IR spectra (Fig. 3B (c)). BD was grafted on the PDA modified stainless steel wire via Michael addition/Schiff base reaction [36], as confirmed by the formation of a new peak at 1654 cm^{-1} corresponded to the C=N band between BD and the PDA on the modified stainless steel wire in the FT-IR spectra (Fig. 3B (b)). In situ growth of TpBD was realized by inserting the BD grafted stainless steel wire into a mixture of Tp, BD, mesitylene, dioxane and acetic acid under certain conditions. The as-grown TpBD shows 2D sheet-like structures (Fig. 2E and F), and characteristic TpBD peaks at 3.3° and 5.8° in the XRD pattern (Fig. 3A (a)) [37], and those of C=N 1654 cm^{-1}, C=C 1571 cm^{-1}, 1450 cm^{-1} and C-N 1288 cm^{-1} in the FT-IR spectra (Fig. 3B (a)). The above results confirm the successful grafting of TpBD on the surface of stainless steel wire. The cross-section image shows about 5 μm thick TpBD coating on the stainless steel wire (Fig. 3D). The TpBD coating is thermally stable until 380 °C (Fig. 3C), which is appropriate for application in GC analysis.

3.2. Optimization of extraction parameters

The effects of various extraction parameters including stirring rate, concentration of NaCl, extraction time and desorption time were investigated in detail.

3.2.1. Effect of stirring rate

The effect of stirring rate was studied at the speed range of 400–800 rpm (Fig. 4A). The peak areas of PAHs significantly increased with stirring rate up to 600 rpm, then gradually levelled off. Generally, fast stirring accelerates the diffusion of the analytes from sample solution to the SPME fiber, which is beneficial for adsorption equilibrium. However, too high stirring speed would cause whirlpool around the SPME fiber, thus unfavorable influence on the stability of SPME. So, the 600 rpm was chosen for the following studies.

3.2.2. Effect of ionic strength

The effect of ionic strength was investigated by changing the concentration of NaCl from 0 to 30% (w/v) (Fig. 4B). The peak areas of eight low-molecular-mass PAHs increased with ionic strength up to 30% due to the decrease of the solubility of nonpolar compounds in the aqueous phase. However, opposite behaviors were observed for the high-molecular-mass PAHs, the extraction efficiency decreased sharply as ionic strength increased due to the increased viscosity of the solution and the decreased diffusion rate of the analytes. Therefore, no salt was added for SPME.

3.2.3. Effect of extraction time and desorption time

The effect of extraction time was evaluated from 20 to 60 min (Fig. 4C). The peak areas of PAHs increased with extraction time up to 50 min, then did not change with further increase of extraction time, indicating that 50 min was sufficient for adsorption equilibrium. Studies on the effect of desorption time, 4 min was enough for quantitative desorption of the PAHs from SPME fiber (Fig. 4D).

3.3. Durability of the TpBD bonded SPME fiber

Extending lifetime of the SPME fiber is a crucial way to overcome the drawback of commercial SPME coating. The developed TpBD bonded SPME fiber can stand at least 200 cycles of adsorption/desorption without significant loss of the extraction efficiency (Fig. S1). In comparison with other reported fibers (Table 2) and conventional commercial fibers (40–100 cycles of adsorption/desorption) [34], the present TpBD bonded SPME fiber offered much longer lifetime due to the high thermal and chemical stability of TpBD and the covalent bond between PDA and TpBD (Fig. 3C, Fig. S2-S3). The high thermal stability of the TpBD bonded fiber also allows the use of high temperature (up to 380 °C) for efficient desorption of the PAHs with high boiling points from the fiber whereas commercial PDMS SPME fiber (30 μm) only permits the maximum temperature of 280 °C for desorption.

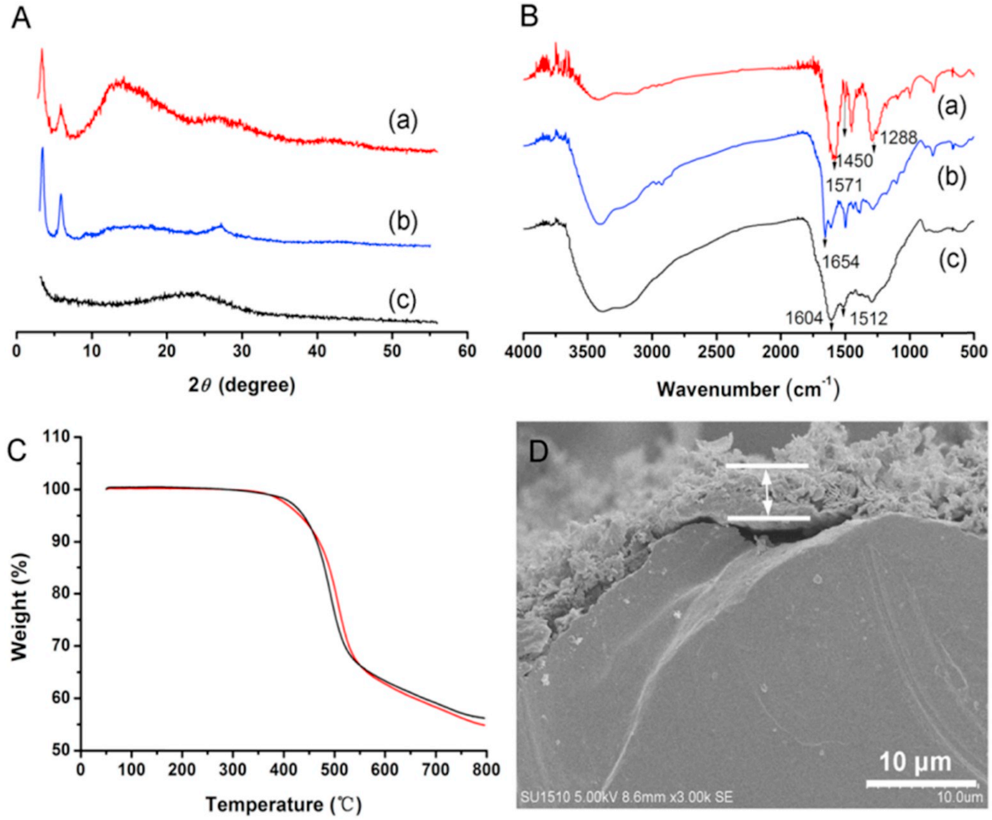

Fig. 3. (A) XRD patterns: (a) the PDA-TpBD coating, (b) TpBD and (c) PDA; (B) FT-IR spectra: (a) the PDA-TpBD coating, (b) PDA-BD and (c) PDA; (C) TGA curves of the TpBD coating (red) and the as-prepared TpBD (black); (D) SEM image of the cross-section of the TpBD bonded SPME fiber. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

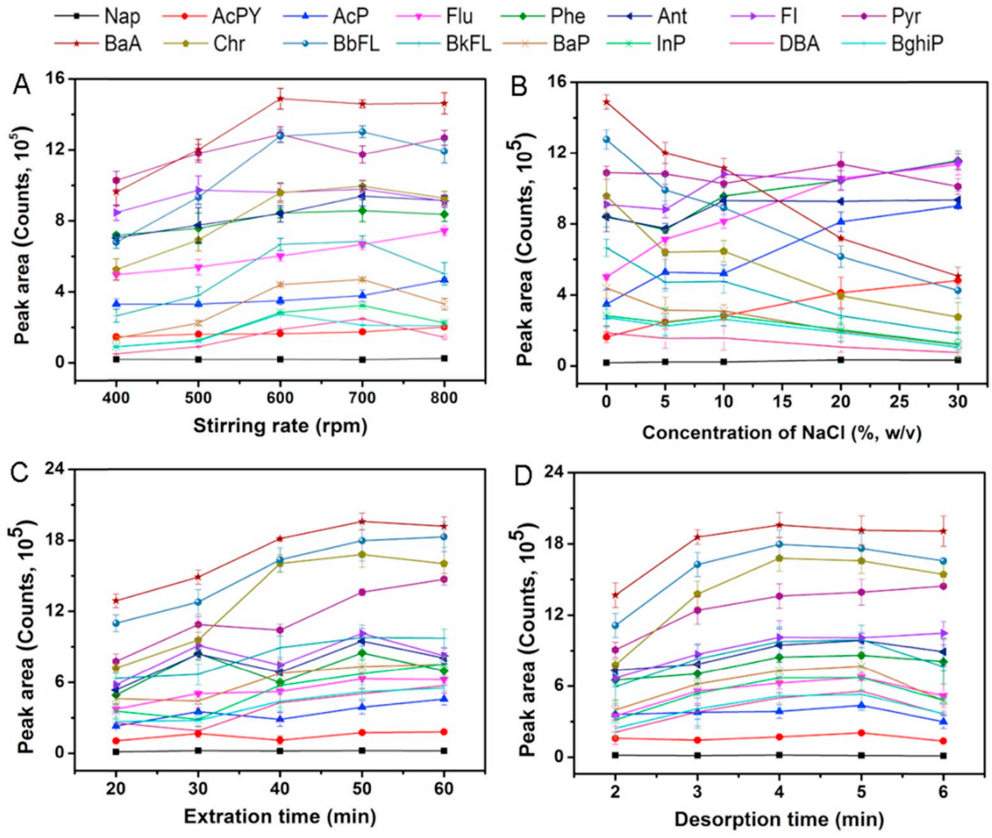

Fig. 4. Effect of experimental conditions on the extraction efficiency for 100 ng L^{-1} PAHs: (A) stirring rate (conditions: extraction time, 30 min; desorption time, 5 min; extraction temperature, 40 °C; no salt addition); (B) concentration of NaCl (conditions: stirring rate, 600 rpm; extraction time, 30 min; desorption time, 5 min; extraction temperature, 40 °C); (C) extraction time (conditions: stirring rate, 600 rpm; desorption time, 5 min; extraction temperature, 40 °C; no salt addition); (D) desorption time (conditions: stirring rate, 600 rpm; extraction time, 50 min and extraction temperature, 40 °C; no salt addition).

Table 1
Analytical performance of the developed method for determination of 16 PAHs.

PAHs	Liner range (ng L^{-1})	R^2	LODs (ng L^{-1})	LOQs (ng L^{-1})	EFs	RSD (%)		
						Intra-day (n = 6)	Inter-day (n = 3)	Fiber to Fiber (n = 3)
NaP	2–200	0.9979	1.66	5.52	1069	7.2	7.8	8.6
AcPy	2–200	0.9981	0.25	0.82	1663	8.5	9.4	10.0
Acp	2–200	0.9982	0.19	0.64	1382	7.8	8.2	9.7
Flu	2–200	0.9986	0.12	0.39	2237	6.1	6.6	6.7
Phe	2–200	0.9931	0.12	0.41	2479	6.9	7.2	8.4
Ant	2–200	0.9966	0.04	0.13	3177	6.3	6.7	6.7
FI	2–200	0.9993	0.03	0.09	3782	5.7	6.4	6.8
Pyr	2–200	0.9950	0.02	0.07	5133	4.3	5.8	6.5
BaA	2–200	0.9919	0.03	0.08	10879	6.0	6.3	6.3
Chr	2–200	0.9987	0.03	0.09	8791	5.5	5.7	5.8
BbFL	2–200	0.9968	0.03	0.08	10346	7.5	8.1	8.2
BkFL	2–200	0.9914	0.04	0.12	9638	5.4	5.6	5.7
BaP	2–200	0.9934	0.07	0.23	6783	5.5	5.7	6.0
InP	2–200	0.9946	0.07	0.23	7300	2.9	4.9	5.3
DBA	2–200	0.9977	0.10	0.33	4616	5.4	5.5	6.5
BghiP	2–200	0.9915	0.10	0.34	4130	2.6	4.5	5.5

Conditions: stirring rate, 600 rpm; extraction time, 50 min; desorption time, 4 min; extraction temperature, 40 °C; no salt addition.

Table 2
Comparison of the developed method with other methods.

SPME coatings	Analytical technique	LODs (ng L^{-1})	Lifetime (cycles)	EFs	Refs
MOF@MON	GC-MS/MS	0.03–0.30	60	1215–3805	[38]
bio-MOF-1	GC-FID	20–5570	–	3104–5980	[39]
MIL-53(Al)	GC-MS/MS	0.10–0.73	150	–	[40]
Graphene	GC-MS	1.52–2.72	–	6354–71872	[8]
UiO-66	GC-MS	0.28–0.60	90	–	[41]
TAPB-TMC-COF	GC-MS	0.29–0.94	–	819–2420	[42]
TpBD	GC-MS/MS	0.02–1.66	200	1069–10879	This work

3.4. Method performance

The analytical performance of our developed method are summarized in Table 1, including linear range (LR), coefficient of determination (R^2), limits of quantification (LOQs), limits of detection (LODs), repeatability, reproducibility and the EFs. The developed method gave a linear range of 2–200 ng L^{-1} for the PAHs with R^2 from 0.9914 to 0.9993. The LODs (S/N = 3) and LOQs (S/N = 10) were in the range of 0.02–1.66 ng L^{-1} and 0.07–5.52 ng L^{-1}, respectively.

The repeatability of the single fiber was obtained by using the TpBD bonded SPME fiber at the concentration of 200 ng L^{-1} for the each of PAHs. The relative standard deviations (RSDs) for intra-day and inter-day study are in the range of 2.6%–8.5% and 4.5%–9.4%, respectively. In addition, the RSDs of fiber-to-fiber for three parallel prepared fibers were in the range of 5.3–10.0%. EF is defined as the ratio of sensitivity after SPME to that obtained by direct injection of 1.0 μL of standard solution. The developed TpBD bonded SPME fiber gave much larger EFs (1069–10879) than PDMS fibers, PDA fibers and etched stainless steel wire (Fig. 5). Moreover, the developed method also gave lower LODs and larger EFs than other SPME based methods (Table 2).

3.5. Application to real samples

The developed method was applied for the determination of trace PAHs in grilled meats with the standard additions method for calibration. Table S2 summarizes the analytical results for the determination of 16 PAHs in the grilled meats by the developed methods. We found Acp, FI, Pyr, BkFL, InP and DBA in the range of 0.39 (DBA) - 2.05 (Pyr) μg kg^{-1} in the mutton shashlik 1, Acp, Flu, FI, Pyr, BkFL, BbFL and InP in the range of 0.38 (BbFL) - 1.54 (Pyr) μg kg^{-1} in the mutton shashlik 2, Acp, Ant, FI, Pyr, BaA, Chr, BkFL, BbFL and InP in the range of 0.37 (BkFL) - 1.54 (Pyr) μg kg^{-1} in the mutton shashlik 3, NaP, FI, Pyr, BaA, Chr, BkFL, DBA and BghiP in a range of 0.46 (BaA) - 1.59 (NaP) μg kg^{-1} in the grilled bacon, and AcPy, Flu, Phe, Ant, FI, Pyr, BaA, Chr, BbFL, BkFL, BaP and InP in a range of 0.11 (Phe) - 1.03 (AcPy) μg kg^{-1} in the grilled chicken wings. Fig. S4 shows the extracted ion chromatograms of the PAHs for real samples. Recoveries obtained by spiking 5, 25 and 50 μg kg^{-1} PAHs in real samples, corresponding to spiking 10, 50 and 100 ng L^{-1} PAHs in working solution, ranged from 85.1 to 102.8% with the RSDs less than 8.4% (n = 6).

4. Conclusions

In summary, we have fabricated an efficient and durable TpBD bonded SPME fiber for SPME-GC-MS/MS determination of 16 PAHs in grilled meat samples with large EFs and low LODs. The large surface area, suitable pore size of the TpBD and the strong π conjugated structure between PAHs and TpBD may account for the superior extraction efficiency for PAHs.

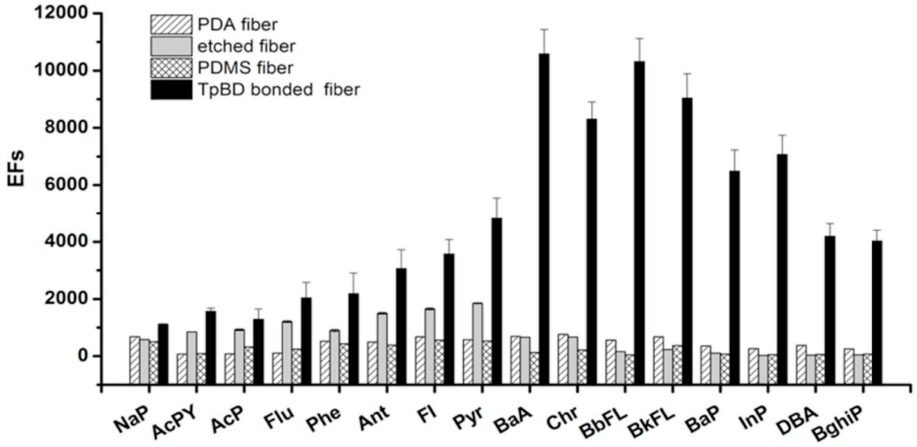

Fig. 5. Comparison of PDA coated fiber, etched fiber, PDMS coated fiber and TpBD bonded fiber for the SPME of the PAHs. Extraction conditions: stirring rate, 600 rpm; extraction time, 50 min; desorption time, 4 min; extraction temperature, 40 °C and no salt addition. For PDMS fiber, the injector temperature was set at 270 °C due to the recommended maximum service temperature of 280 °C.

Notes

The authors declare no competing financial interest.

Acknowledgements

This work was supported by National Key R&D Program of China (2018YFC1602300), the National Natural Science Foundation of China (21775056), the Fundamental Research Funds for the Central Universities (JUSRP51714B), and the National First-class Discipline Program of Food Science and Technology (JUFSTR20180301).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2019.04.031.

References

[1] J. Bouhlel, D.J.R. Bouveresse, S. Abouelkaram, E. Baéza, C. Jondreville, A. Travel, J. Ratel, E. Engel, D.N. Rutledge, Comparison of common components analysis with principal components analysis and independent components analysis: application to SPME-GC-MS volatolomic signatures, Talanta 178 (2018) 854–863.

[2] S.H. Huo, X.P. Yan, Facile magnetization of metal-organic framework MIL-101 for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons in environmental water samples, Analyst 137 (2012) 3445–3451.

[3] L.L.A. Veiga, H. Amorim, J. Moraes, M.C. Silva, R.S.L. Raices, S.L. Quiterio, Quantification of polycyclic aromatic hydrocarbons in toasted guaraná (Paullinia cupana) by high-performance liquid chromatography with a fluorescence detector, Food Chem. 152 (2014) 612–618.

[4] ATSDR, Toxicology Profile for Polyaromatic Hydrocarbons. ATS-DR's Toxicological Profiles on CD-ROM, CRC Press, Boca Raton, FL, 2005.

[5] Administrative Committee of the Federal Register, Electronic Code of Federal Regulations, Title 21: Food and Drugs, Chapter I, Subpart B-Requirements for Specific Standardized Beverages, (2018) Part 165 https://www.ecfr.gov/cgi-bin/text-idx?SID=6ab26df94caa71dc5b2daf5c2ad9df38&mc=true&node=pt21.2.165&rgn=div5.

[6] EC European Commission, Commission Regulation (EU) No 835/2011 of 19 August 2011 Amending Regulation (EC) No 1881/2006 as Regards Maximum Levels for Polycyclic Aromatic Hydrocarbons in Foodstuffs, (2011) http://eur-lex.europa.eu/legalcontent/EN/TXT/?qid¼14764248974.44&uri¼CELEX:32011R0835.

[7] S.H. Zhang, Q. Yang, Z. Li, W.J. Wang, X.H. Zang, C. Wang, Z. Wang, Solid phase microextraction of phthalic acid esters from vegetable oils using iron (III)-based metal-organic framework/graphene oxide coating, Food Chem. 263 (2018) 258–264.

[8] S.L. Zhang, Z. Du, G.K. Li, Layer-by-Layer fabrication of chemical-bonded graphene coating for solid-phase microextraction, Anal. Chem. 83 (2011) 7531–7541.

[9] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 62 (1990) 2145–2148.

[10] C.L. Rainey, D.E. Bors, J.V. Goodpaster, Design and optimization of a total vaporization technique coupled to solid-phase microextraction, Anal. Chem. 86 (2014) 11319–11325.

[11] D. Martin, J. Ruiz, Analysis of polycyclic aromatic hydrocarbons in solid matrixes by solid-phase microextraction coupled to a direct extraction device, Talanta 71 (2007) 751–757.

[12] A. Derouiche, M.R. Driss, J.P. Morizur, M.H. Taphanel, Simultaneous analysis of polychlorinated biphenyls and organochlorine pesticides in water by headspace solid-phase microextraction with gas chromatography-tandem mass spectrometry, J. Chromatogr. A 1138 (2007) 231–243.

[13] J.N. Bianchin, G. Nardini, J. Merib, A.N. Dias, E. Martendal, E. Carasek, Simultaneous determination of polycyclic aromatic hydrocarbons and benzene, toluene, ethylbenzene and xylene in water samples using a new sampling strategy combining different extraction modes and temperatures in a single extraction solid-phase microextraction-gas chromatography-mass spectrometry procedure, J. Chromatogr. A 1233 (2012) 22–29.

[14] N. Aguinaga, N. Campillo, P. Viñas, M. Hernández-Córdoba, Determination of 16 polycyclic aromatic hydrocarbons in milk and related products using solid-phase microextraction coupled to gas chromatography-mass spectrometry, Anal. Chim. Acta 596 (2007) 285–290.

[15] F.J. Uribe-Romo, J.R. Hunt, H. Furukawa, C. Klöck, M. O'Keeffe, O.M. Yaghi, A crystalline imine-linked 3-D porous covalent organic framework, J. Am. Chem. Soc. 131 (2009) 4570–4571.

[16] H.M. El-Kaderi, J.R. Hunt, J.L. Mendoza-Cortés, A.P. Côté, R.E. Taylor, M. O'Keeffe, O.M. Yaghi, Designed synthesis of 3D covalent organic frameworks, Science 316 (2007) 268–272.

[17] S. Kandambeth, A. Mallick, B. Lukose, M.V. Mane, T. Heine, R. Banerjee, Construction of crystalline 2D covalent organic frameworks with remarkable chemical (Acid/Base) stability via a combined reversible and irreversible route, J. Am. Chem. Soc. 134 (2012) 19524–19527.

[18] S. Chandra, S. Kandambeth, B.P. Biswal, B. Lukose, S.M. Kunjir, M. Chaudhary, R. Babarao, T. Heine, R. Banerjee, Chemically stable multilayered covalent organic nanosheets from covalent organic frameworks via mechanical delamination, J. Am. Chem. Soc. 135 (2013) 17853–17861.

[19] H.L. Qian, C.X. Yang, W.L. Wang, C. Yang, X.P. Yan, Advances in covalent organic frameworks in separation science, J. Chromatogr. A 1542 (2018) 1–18.

[20] J. Li, X.D. Yang, C.Y. Bai, Y. Tian, B. Li, S. Zhang, X.Y. Yang, S.D. Ding, C.Q. Xia, X.Y. Tan, L.J. Ma, S.J. Li, A novel benzimidazole-functionalized 2-D COF material: synthesis and application as a selective solid-phase extractant for separation of uranium, J. Colloid Interface Sci. 437 (2015) 211–218.

[21] G.Y. Lee, J. Lee, H.T. Vo, S. Kim, H. Lee, T. Park, Amine-Functionalized covalent organic framework for efficient SO_2 capture with high reversibility, Sci. Rep. 7 (2017) 1–10.

[22] W.C. Wang, J.T. Wang, S.H. Zhang, P.L. Cui, C. Wang, Z. Wang, A novel Schiff base network-1 nanocomposite coated fiber for solid-phase microextraction of phenols from honey samples, Talanta 161 (2016) 22–30.

[23] N. Li, D. Wu, N. Hu, G.S. Fan, X.T. Li, J. Sun, X.F. Chen, Y.R. Suo, G.L. Li, Y.N. Wu, Effective enrichment and detection of trace polycyclic aromatic hydrocarbons in food samples based on magnetic covalent organic framework hybrid microspheres, J. Agric. Food Chem. 66 (2018) 3572–3580.

[24] T. Wu, X.H. Zang, M.T. Wang, Q.Y. Chang, C. Wang, Q.H. Wu, Z. Wang, Covalent organic framework as fiber coating for solid-phase microextraction of chlorophenols followed by quantification with gas chromatography-mass spectrometry, J. Agric. Food Chem. 66 (2018) 11158–11165.

[25] Q. Sun, B. Aguila, J. Perman, N. Nguyen, S.Q. Ma, Flexibility matters: cooperative active sites in covalent organic framework and threaded ionic polymer, J. Am. Chem. Soc. 138 (2016) 15790–15796.

[26] H. Xu, J. Gao, D.L. Jiang, Stable, crystalline, porous, covalent organic frameworks as a platform for chiral organocatalysts, Nat. Chem. 7 (2015) 905–912.

[27] Y.W. Peng, M.T. Zhao, B. Chen, Z.C. Zhang, Y. Huang, F.N. Dai, Z.C. Lai, X.Y. Cui, C.L. Tan, H. Zhang, Hybridization of MOFs and COFs: a new strategy for construction of MOF@COF core-shell hybrid materials, Adv. Mater. 30 (2018) 1705454.

[28] Z.M. Yan, J.N. Zheng, J.F. Chen, P. Tong, M.H. Lu, Z.A. Lin, L. Zhang, Preparation and evaluation of silica-UIO-66 composite as liquid chromatographic stationary phase for fast and efficient separation, J. Chromatogr. A 1366 (2014) 45–53.

[29] L.L. Wang, C.X. Yang, X.P. Yan, In situ growth of covalent organic framework shells on silica microspheres for application in liquid chromatography, ChemPlusChem 82 (2017) 933–938.

[30] H.L. Qian, C. Dai, C.X. Yang, X.P. Yan, High-crystallinity covalent organic framework with dual fluorescence emissions and its ratiometric sensing application, ACS Appl. Mater. Interfaces 9 (2017) 24999–25005.

[31] C.J. Zhang, G.K. Li, Z.M. Zhang, A hydrazone covalent organic polymer based micro-solid phase extraction for online analysis of trace Sudan dyes in food samples, J. Chromatogr. A 1419 (2015) 1–9.

[32] S.H. Zhang, Q. Yang, Z. Li, W.C. Wang, C. Wang, Z. Wang, Covalent organic frameworks as a novel fiber coating for solid-phase microextraction of volatile benzene homologues, Anal. Bioanal. Chem. 409 (2017) 3429–3439.

[33] L. Chen, M.Y. Zhang, F.F. Fu, J.G. Li, Z.A. Lin, Facile synthesis of magnetic covalent organic framework nanobeads and application to magnetic solid-phase extraction of trace estrogens from human urine, J. Chromatogr. A 1567 (2018) 136–146.

[34] M.X. Wu, G. Chen, J.T. Ma, P. Liu, Q. Jia, Fabrication of cross-linked hydrazone covalent organic frameworks by click chemistry and application to solid phase microextraction, Talanta 161 (2016) 350–358.

[35] Y. Li, C.X. Yang, C.X. Yang, Controllable preparation of core-shell magnetic covalent-organic frameworknanospheres for efficient adsorption and removal of bisphenols in aqueous solution, Chem. Commun. 53 (2017) 2511–2514.

[36] L.Q. Xu, W.J. Yang, K.G. Neoh, E.T. Kang, G.D. Fu, Dopamine-induced reduction and functionalization of graphene oxide nanosheets, Macromolecules 43 (2010) 8336–8339.

[37] C.X. Yang, C. Liu, Y.M. Cao, X.P. Yan, Facile room-temperature solution-phase synthesis of a spherical covalent organic framework for high-resolution chromatographic separation, Chem. Commun. 51 (2015) 12254–12257.

[38] Y.Q. Jia, H. Su, Z.H. Wang, Y.L.E. Wong, X.F. Chen, M.L. Wang, T.W.D. Chan, Metal-organic Framework@Microporous organic network as adsorbent for solid-phase microextraction, Anal. Chem. 88 (2016) 9364–9367.

[39] S.H. Huo, J. Yu, Y.Y. Fu, P.X. Zhou, In situ hydrothermal growth of a dual-ligand metal-organic framework film on a stainless steel fiber for solid-phase microextraction of polycyclic aromatic hydrocarbons in environmental water samples, RSC Adv. 6 (2016) 14042–14048.

[40] X.F. Chen, H. Zang, X. Wang, J.G. Cheng, R.S. Zhao, C.G. Cheng, X.Q. Lu, Metal-organic framework MIL-53(Al) as a solid-phase microextraction adsorbent for the determination of 16 polycyclic aromatic hydrocarbons in water samples by gas chromatography-tandem mass spectrometry, Analyst 137 (2012) 5411–5419.

[41] J. Gao, C.H. Huang, Y.F. Lin, P. Tong, L. Zhang, In situ solvothermal synthesis of metal-organic framework coated fiber for highly sensitive solid-phase microextraction of polycyclic aromatic hydrocarbons, J. Chromatogr. A 1436 (2016) 1–8.

[42] X.M. Yang, J.M. Wang, W.J. Wang, S.H. Zhang, C. Wang, J.H. Zhou, Z. Wang, Solid phase microextraction of polycyclic aromatic hydrocarbons by using an etched stainless-steel fiber coated with a covalent organic framework, Microchim. Acta 186 (2019) 145–152.