

Solid-phase microextraction coatings based on the metal-organic framework ZIF-8: ensuring stable and reusable fibers

Priscilla Rocío-Bautista¹, Adrián Gutierrez-Serpa¹, Alexander John Cruz², Rob Ameloot², Juan H. Ayala¹, Ana M. Afonso¹, Jorge Pasán³, Sabina Rodríguez-Hermida^{2*}, Verónica Pino^{1,4**}

¹*Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), La Laguna, Tenerife, 38206 Spain*

²*Centre for Membrane Separations, Adsorption, Catalysis, and Spectroscopy for Sustainable Solutions (cMACS), Department of Microbial and Molecular Systems, KU Leuven, Leuven, 3001 Belgium*

³*Departamento de Física, Laboratorio de Rayos X y Materiales Moleculares, Universidad de La Laguna (ULL), La Laguna, Tenerife, 38206 Spain*

⁴*Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias, Universidad de La Laguna (ULL), La Laguna, Tenerife, 38206 Spain*

Abstract

Chemical vapour deposition of MOFs (MOF-CVD) has been used to coat solid-phase microextraction (SPME) fibers with ZIF-8, by exposing ZnO layers to the linker vapor (2-methylimidazole). This ZIF-8 coating has been used as a seed layer in a following solvothermal MOF growth step in order to increase the ZIF-8 thickness. The combined MOF-CVD and solvothermal growth of ZIF-8 on the fibers result in a thickness of $\sim 3\ \mu\text{m}$, with adequate thermal stability, and mechanical integrity when tested with methanol ultrasonic treatments. The fibers have been tested in direct immersion and headspace modes using gas chromatography and flame ionization detection (GC-FID), for a group of target analytes including three polycyclic aromatic hydrocarbons and five personal care products. The optimized conditions of the SPME-GC-FID methods include low amount of aqueous sample (5 mL), stirring for 45 min at 35 °C, and desorption at 280 °C for 5 min. The method presents limits of detection down to $0.6\ \mu\text{g}\cdot\text{L}^{-1}$; intra-day, inter-day and inter-batch relative standard deviation values lower than 16%, 19%, and 23%, respectively; and a lifetime higher than 70 cycles.

Keywords: metal-organic frameworks; solid-phase microextraction; fibers; new coatings; chemical vapor deposition; atomic layer deposition; analytical sample preparation

****Corresponding author:** Tel. +34 922318990. Email: veropino@ull.edu.es

***Co-corresponding author:** Tel. +32 016372782. Email: sabina.rodriquezhermida@kuleuven.be

P. Rocio-Bautista procio@ull.edu.es

A. Gutiérrez-Serpa agutiers@ull.edu.es

A.J. Cruz alex.cruz@kuleuven.be

J.H. Ayala jhayala@ull.edu.es

A.M. Afonso aafonso@ull.edu.es

J. Pasán jpasang@ull.edu.es

R. Ameloot rob.ameloot@kuleuven.be

1. Introduction

Solid-phase microextraction (SPME) is an advantageous method in analytical extraction and pre-concentration schemes, due to its robustness, simplicity, fastness, and sensitivity. As an organic solvent-free procedure, SPME is regarded as environmentally friendly in gas chromatography (GC) applications [1,2]. Despite its success in a variety of (bio)analytical sample preparation fields [3-5], commercially available coatings for SPMEs are limited. Therefore, the field focuses on the development of new coating materials [6-10] such as mesoporous silica [11], carbon nanomaterials [12,13], metal and metal oxides nanoparticles [14,15], molecularly-imprinted polymers [16,17], and more recently, metal-organic frameworks (MOFs) [18-22].

MOFs are coordination polymers based on metal nodes and multitopic organic linkers, exhibiting impressive specific surface areas [23,24]. Crystalline MOFs are characterized by their uniformly structured nanoscale cavities and pore topologies, high adsorption affinity, and chemical tunability [25] for the pore environment and the outer-surface [26,27]. In addition, it is possible to design low cytotoxic and water-stable MOFs [28,29]. Due to their intrinsic properties, MOFs have been very attractive as highly-efficient materials in analytical chemistry [20,30], with SPME not being an exception for their applicability [18].

To obtain robust MOF-based SPME coatings, adhesion of the crystals to the fiber support is required. Metallic fibers are normally pre-treated by etching with acids to generate rough surfaces [31,32]. The most common route to prepare MOF-based SPME fibers requires liquid-based methods; by immersing the pre-treated support in the MOF precursors' solution under adequate temperature, time, and pressure conditions [31,33-36]. The MOF-based fibers obtained with this procedure are commonly utilized in headspace SPME (HS-SPME) analysis [35-38] because the weak MOF-to-support anchorage complicates direct immersion (DI) applications. To date, MOF-based fibers in DI-SPME applications show low reusability unless they are included in complex composites, with the MOF not being the unique sorbent material of the coating [34-39]. Therefore, better routes to immobilize MOFs to SPME supports are necessary to improve their applicability in DI applications.

The chemical vapor deposition of MOFs (MOF-CVD), a novel route to fabricate MOF thin films, is based on a two-step process by first depositing the metal precursor layer and then exposing it to a sublimed organic linker, resulting in thin, homogeneous,

crystalline and porous MOF films [40-45]. This method has been demonstrated for the deposition of different MOFs, such as ZIF-8 or ZIF-67, isorecticular microporous 3D-MOFs based on Zn(II) or Co(II) ions connected by 2-methylimidazolate linkers [44,46], and has recently been scaled up as an integrated cleanroom process [47]. The MOF-CVD method has also been successfully expanded to new MOF chemistries, such as the deposition of Cu-carboxylate [48] and Zn-triazolate framework films [49].

If a combined MOF-CVD and solvothermal method is used, the MOF-CVD layer can provide strongly-anchored nucleation points for crystals formed during the solvothermal growth step. This two-step strategy also enhances the binding of the MOF to the fiber support. This concept has been recently described for thick UiO-66 SPME coatings, showing adequate extraction capability for phenols in wastewaters mostly using HS-SPME but also applying DI- with blade and arrow type SPME configurations [50]. However, the preparation of such coatings has been studied only for these two type of devices (blade and arrow), which have higher anchoring surface. Here, we show the use of this two-step strategy for the deposition of ZIF-8 on more conventional fibers for SPMEs in DI applications.

2. Experimental

2.1. Chemicals, reagents, materials, and samples

The studied PAHs included acenaphthene (Ace), fluorene (Fl), and pyrene (Py), supplied as solids with 98% purity by Aldrich (Milwaukee, Wisconsin, USA). The studied PCPs included homosalate (HMS) (99%), 2-ethylhexylsalicilate (EHS) (98%), methyl-antralinate (MA) (98.5%), padimate-O (OD-PABA) (98%), and ethylhexyl 4-methoxycinnamate (EHMC) (98%), and were acquired to Sigma-Aldrich (Steinheim, Germany). The main characteristics of target analytes are included in Table S1 of the Electronic Supplementary Material (ESM).

Standard solutions containing all analytes at a concentration of 10 mg·L⁻¹ were prepared in acetonitrile (ACN) HiPerSolv Chromanorm® liquid chromatography (LC) grade, purchased from VWR (Llinars del Vallés, Spain). Working standard solutions were prepared weekly in ACN at concentrations of 1 mg·L⁻¹, and stored at 4 °C while protected

from light. Aqueous standard solutions were prepared daily, using ultrapure water at concentrations ranging from 1.0 to 100 $\mu\text{g}\cdot\text{L}^{-1}$ for the SPME calibrations (the acetonitrile content in these aqueous solutions was always lower than 0.5% v/v), and at 100 $\mu\text{g}\cdot\text{L}^{-1}$ in the optimization studies. Ultrapure Milli-Q water was obtained by a water purification system A10 MilliPore (Watford, UK).

Metal alloy polished wire (135 μm as diameter) was used as SPME fiber support, being supplied by Nitinol Devices & Components (Fremont, CA, USA).

Reagents included in the preparation of the ZIF-8 based SPME fibers were: sodium formate (99%), supplied by Fisher Scientific (Hampton, New Hampshire, USA), 2-methylimidazole (2-MIm) (>98%) and methanol with pure quality, obtained from Sigma-Aldrich, and zinc nitrate monohydrate ($\text{Zn}(\text{NO}_3)_2\cdot\text{H}_2\text{O}$, 98%, ultrapure quality), purchased to Acros Organics (Geel, Belgium). The diethylzinc (97%) precursor for the atomic layer deposition process (ALD) was acquired from STREM Chemicals, Inc. (Newburyport, MA, USA).

The solvothermal synthesis of ZIF-8 onto the fibers was performed in Pyrex® glass bottles of 30 and 50 mL (Staffordshire, UK).

The DI-SPME studies were carried out in amber glass vials of 7 mL with septum caps supplied by Agilent Technologies (Santa Clara, CA, USA). For comparison, the commercial SPME fibers supplied by Supelco (Bellefonte, PA, USA): polyacrylate (PA) with a thickness of 85 μm and polydimethylsyloxane (PDMS) with a thickness of 100 μm , were used. Brand® polytetrafluoroethylene (PTFE) magnetic stir bars 7×2 mm were acquired from Sigma-Aldrich.

Two wastewater samples from a sewage treatment plant (WWTP) in Puerto de la Cruz and from a wastewater pumping station (WWPS) in Santa Cruz de Tenerife were analyzed. Samples were collected in 1 L glass bottles, protected from the light, kept in portable fridges, and stored at 4 °C in the laboratory. Samples were filtered through 0.2 μm PTFE filters before their analysis.

All glassware, including the vials, were washed with detergent and tap water, followed by washing with 1:10 (v/v) of nitric acid purchased to Panreac (Barcelona, Spain) and deionized water. Finally, non-graduated glassware and vials were heated in a muffle furnace at 550 °C for 3 h to ensure full removal of organic matter.

2.2. Instruments and equipment

Phase identification of the as-synthesized ZIF-8 was carried out by X-ray powder diffraction using an X'Pert PRO Multi-Purpose Diffractometer (PANalytical, Netherlands) operating with Bragg-Brentano geometry. Data collection was carried out using Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) over the angular range from 5.01° to 50.00° with a total data acquisition time of 20 min. The Si-witness samples were characterized by grazing incident X-ray diffraction (GIXRD) using a Malvern PANalytical Empyrean diffractometer equipped with a PIXcel3D solid state detector using a Cu anode. The GIXRD patterns were recorded at room temperature in reflection geometry (Bragg-Brentano) with an incident beam angle of 0.02° . The attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) spectra were recorded on a Varian 670 FTIR spectrometer equipped with a VeeMAX III accessory, with a Ge ATR crystal.

The ALD system for the deposition of ZnO was a Savannah S-200, from Veeco Instruments Inc. (Waltham, MA, USA) using the established protocol [47]. To measure the ALD ZnO film thickness on the witness Si wafer, M2000x spectroscopic ellipsometry from J.A. Woollam Co., Ltd. Company (Lincoln, NE, USA) was used. The ellipsometer instrument was operated at an incident angle of 70° covering a wavelength range of 246-1000 nm.

The microscopic images of the SPME fibers were obtained by a scanning electronic microscope (SEM) JSM-6010LV from JEOL (Tokyo, Japan), supporting the fiber on a flat surface with a silver cover. Further studies regarding the morphology and elemental composition of the MOF-based coating were determined using a scanning electron microscope (SEM) Zeiss EVO15 (Carl Zeiss AG, Heidenheim, Germany) equipped with an energy dispersive X-ray analyzer (EDX).

Chromatographic analyses were performed in a GC coupled to a flame ionization detector (FID) Varian 450 CP3800 model (Palo Alto, CA, USA). The chromatographic column was a Factor Four Capillary Column VF-5ms ($30 \text{ m} \times 250 \text{ }\mu\text{m} \times 0.25 \text{ }\mu\text{m}$) from Agilent. The carrier gas was nitrogen at $1 \text{ mL}\cdot\text{min}^{-1}$. The optimum GC oven temperature program started at 70°C , then increased up to 190°C at $8^\circ\text{C}\cdot\text{min}^{-1}$, then increased up to 195°C at $4^\circ\text{C}\cdot\text{min}^{-1}$, being held for 2 min, and finally raised up to 300°C at $15^\circ\text{C}\cdot\text{min}^{-1}$, and kept isothermally for additional 4 min. The injector temperature was kept at 280°C , and the working temperature of the detector was 280°C . The FID flame required a flow of air of $300 \text{ mL}\cdot\text{min}^{-1}$, nitrogen (*make-up*) flow of $30 \text{ mL}\cdot\text{min}^{-1}$, and hydrogen flow of

30 mL·min⁻¹. Star Chromatography Workstation version 6.20 software (also from Varian) was used for data acquisition and analysis.

The ultrasound bath was a Sonorex Digitec, from Bandelin electronic GmbH & Co. KG (Berlin, Germany).

2.3. Preparation of SPME fibers based on ZIF-8

The metal alloy wires were first cleaned using acetone and ultrasonic treatment for 10 min. Then, MOF-CVD and solvothermal methods were used to deposit the ZIF-8 layer. A witness Si wafer was subjected to the same procedures to facilitate further characterization. The entire ZIF-8 deposition procedure starts by deposition of the ZIF-8 through MOF-CVD followed by its solvothermal growth.

2.3.1. MOF-CVD deposition of ZIF-8

Atomic layer deposition of ZnO: 10 nm of ZnO was deposited by the alternating reactions of deionized water and diethylzinc (DEZ, 97%, STREM) with nitrogen (99.999%) as the carrier and purging gas. The pulse and purge durations for the ALD precursors were set to 0.015 s and 5 s, respectively. The reactor base pressure was ~ 0.40 mbar at an N₂ gas flow of 20 sccm at 80 °C. The coated metal alloy wires were cut into 6 cm pieces and partially covered with Teflon tape in order to have only 2 cm length expose to the next steps.

ZnO-to-ZIF-8 conversion through solid-vapor reaction: The ZnO coated nitinol fibers were exposed to 2-MIm vapor for 1 h at 120 °C. Afterward, the fibers were thermally activated at 150 °C for 30 min to remove the excess of the linker. This approach ensures the formation of the ~100 nm ZIF-8 layer.

2.3.2. Solvothermal ZIF-8 growth.

The fibers were immersed in a solution containing the ZIF-8 precursors: 5 mmol of Zn(NO₃)₂·H₂O, 40 mmol of 2-MIm, 1 mmol of sodium formate as a stabilizer and 40 mL of MeOH. The mixture was heated at 60 °C for 24 h. This procedure was repeated one more time, with the obtained fibers placed again in a fresh solution of ZIF-8 precursors.

2.4. DI-SPME-GC-FID analyses

Under optimum conditions, DI-SPME-GC-FID experiments were carried out directly exposing 1 cm of the coated fiber to the aqueous solution (5 mL, with the concentration depending on the specific experiment) of the target analytes – or to the aqueous sample – in 7 mL vials under magnetic stirring at 500 rpm for 45 min at 35 °C. The temperature of the vials was kept constant using a basic heater from Kika®Werke (Staufen, Germany). Afterward, the fiber is retracted in the SPME holder and then exposed to thermal desorption in the GC injector, at 280 °C for 5 min, to start the GC-FID analysis. Desorption temperature and timing ensured the absence of memory effects. PA and PDMS fibers were utilized in the same manner for comparative purposes.

3. Results and discussion

3.1. MOF-CVD deposition of ZIF-8 layer onto the metal alloy support

First, a layer of ~10 nm of ALD ZnO was selected as the precursor thickness for ZIF-8 MOF-CVD conversion to ensure sufficient nucleation points for the next deposition steps. After the deposition of the metal precursor layer on the metal alloy wire, it was cut into 6 cm pieces. Teflon tapers covered these pieces leaving only 2 cm exposed to CVD [47].

The CVD method was accomplished in Petri dishes containing the 2-MIm ligand (as solid powder). A plate was placed over it while heating at 120 °C for 20 min, thus ensuring an excess of the ligand vapors in such space. Afterward, the fibers were put in contact with such vapors for 1 h at 120 °C. This procedure ensures the formation of a ZIF-8 layer in less than 1 min, being the growth of this layer time-dependent [42]. Profilometry studies performed on ZnO-deposited silicon wafers (before and after CVD) show a 10 time-thickness increase after CVD. Figures S1 and S2 of the ESM compiles the characterization performed to the Si-witness samples. Therefore, the estimated thickness of ZIF-8 onto the wires after the entire ALD-CVD method is ~100 nm. These fibers were activated subsequently by heating at 150 °C for 30 min to ensure the removal of any non-reacted linker. Figure 1 shows a scheme of the entire procedure.

3.2. Solvothermal growth of ZIF-8 onto the ZIF-8 coated SPME fiber

Once the fibers were coated with ~ 100 nm ZIF-8 through the MOF-CVD method, these were immersed in a solution containing the ZIF-8 precursors to obtain a thicker MOF layer. Different reaction times were used for the solvothermal step: 24 h, 48 h, and 2×24 h (in the latter case using a fresh reaction medium the second day). After 24 h reaction time, the wire is homogeneously coated, while longer reaction time (48 h) led to unequal distribution of crystallites. The best strategy to obtain a homogeneous coating of *ca.* 3 μm thickness is using a 2 x 24 h reaction time (Figure S3 of the ESM). Figure S4 and S5 of the ESM show images of the coating thickness under optimum conditions. The excess powder formed in the vials was characterized by PXRD, indicating the formation of the ZIF-8 structure (Figure S6 of the ESM).

To evaluate the coating adhesion, the fibers were immersed in different organic solvents (methanol and acetonitrile, those most widely involved in chromatographic applications), and ultrasonicated for 10 min. The coated fibers were also heated for 5 – 10 min at 280 °C, to mimic common GC applications. In all cases, there were no significant morphological modifications in the surface of the coatings, as it can be observed in Figure S7 of the ESM.

3.3. Optimization of the DI-SPME-GC-FID method using ZIF-8-based SPME coatings

We have first evaluated the influence of the different main factors on the DI-SPME-GC performance, such as extraction and desorption time of the fibers, extraction temperature and stirring strength. For that, the extraction efficiency of each target analyte was monitoring as peaks areas (Figure S8 of the ESM). The remaining variables were fixed during the one-factor-at-a-time optimization study: 5 mL of the aqueous standard (5 to 20 mL are the most commonly used volumes in this technique), the maximum desorption temperature in the GC injector for ZIF-8 (280 °C), and the concentration of the aqueous standard ($100\ \mu\text{g}\cdot\text{L}^{-1}$).

The extraction time profiles were obtained using an extraction temperature of 25 °C, and 500 rpm stirring for 15, 30, 45, 60, and 75 min. and GC desorption conditions of 280 °C for 5 min in all cases. Figure S8 (A) of the ESM shows an improvement in the extraction efficiency for all target analytes at 45 min (and over) with the exception of Ace, and thus this extraction time was selected as optimum. Once fixed this optimal extraction time, the desorption time was also evaluated to guarantee the absence of carry-over and to maximize efficiency. Thus, at room temperature, 500 rpm of stirring, and 45

min of extraction time, the tested desorption times were: 2, 5, 10, 15, and 20 min. From Figure S8 (B) of the ESM, it is clear that 5 min is more than enough to obtain an adequate desorption efficiency for all compounds while avoiding carry-over in further blank analyses. Figure S8 (C) of the ESM includes the analytical performance when different stirring rates (from 200 to 600 rpm) were tested under the conditions already set. This parameter was not significant for Ace, DEET, Flu, and MA. In any case, values between 500 and 600 rpm were efficient for most analytes, thus selecting 500 rpm as optimum. The last parameter optimized in the DI-SPME-GC procedure was the extraction temperature, as included in Figure S8 (D) of the ESM, being 35 °C the best temperature. In summary, the optimum conditions include direct immersion of 1 cm of the ZIF-8 based SPME fiber in 5 mL of the sample at 35 °C and 500 rpm for 45 min, followed by desorption in the GC injector at 280 °C during 5 min.

3.4. DI-SPME-GC-FID analytical method performance with ZIF-8-based SPME coatings

The analytical performance of the DI-SPME-GC-FID method using ZIF-8 based SPME coatings was evaluated with aqueous standards subjected to the entire method. Table 1 shows several quality analytical parameters of the method. The obtained calibrations presented in all cases determination coefficient values (R) higher than 0.995. Limits of detection (LODs) were calculated as three times the signal to noise ratio. Aqueous standards prepared at those levels (and subjected to the entire method) served to verify experimentally the obtained LODs, which range from 0.6 $\mu\text{g}\cdot\text{L}^{-1}$ for EHS to 2.0 $\mu\text{g}\cdot\text{L}^{-1}$ for Ace.

Table 2 includes a comparison of the analytical performance with a group of neat MOF-based SPME fibers from literature, in all cases using DI-SPME-GC for water analysis. In order to focus the comparison on the MOF nature and its link to the SPME support, other studies using composites based on MOFs, hence containing different extraction materials in the coating were excluded. Clearly, MOF-based fibers are able to operate at common extraction temperatures, between 20 min and 1 h (45 min in the present study). Taking into account the known thermal stability of MOFs, these materials are interesting for GC applications. With regards to the analytical performance, sensitivity has been checked with mass spectrometry (MS) in the studies reported [39,50], being FID in the current study, thus justifying the differences in LODs obtained. Furthermore, lighter PAHs have been the ones studied with ZIF-8 and heavier PAHs those included in the study with bioMOF-102 [39]. It is also important to mention that the thicker coating

is obtained with the bioMOF-102, prepared by two consecutive post-synthetic modifications starting from bioMOF-100. Therefore, a long preparation time is needed (four days). In the present study, both PAHs and PCPs have been tested, thus scrutinizing analytes with a broad chemical nature; while in the reported works, the studied applications are devoted to analytes belonging to the same family of compounds [50], or compounds with similar structures [39].

Precision was evaluated as relative standard deviation (in %) using ZIF-8 based SPME coatings with intra-day studies ($n = 4$), inter-day studies ($n = 3$ in each day, for 3 non-consecutive days), and inter-batch studies ($n = 3$ intra-day, for 3 different SPME coatings). The aqueous standard used to assess validation was $50 \mu\text{g}\cdot\text{L}^{-1}$. Intra- and inter-day RSD presented values lower than 16 and 19% respectively, which is in agreement with MOFs performance in SPME (Table 2). The observed inter-batch RSD values range from 17 to 23%, which is highly adequate and shows the reproducibility and uniformity of the coatings obtained with this procedure, despite their use in DI- mode. Literature studies with neat MOF-based coatings for DI-SPME do not report studies of inter-batch precision. Inter-batch precision should be reported when proposing new materials for analytical microextraction approaches.

Regarding the reusability of the novel ZIF-8 based SPME coatings, working under DI- conditions, the number of extraction cycles was approximately 70, which should be highlighted considering the common fragility associated with MOF crystals in SPME.

To evaluate the analytical performance of the ZIF-8 based fibers when dealing with these complex media, real wastewaters samples were also analyzed. Sample 1 came from a WWTP in Puerto de la Cruz (Tenerife) and Sample 2 from a WWPS in Santa Cruz de Tenerife. Samples were analyzed in triplicate under the optimum extraction conditions. None of the studied analytes was detected in the samples, and thus they were spiked at $50 \mu\text{g}\cdot\text{L}^{-1}$ with the analytes in order to estimate possible matrix effect in terms of relative recoveries (RR). Table S2 of the ESM includes the results for each sample. Regarding wastewater Sample 1, the RR values clearly increase, while decreasing in Sample 2. In both cases, strong matrix effects are present. Regarding the intra-day RSD values obtained, they were lower than 23% for Sample 1 and lower than 20% for Sample 2, thus showing adequate precision despite matrix complexity. After these studies, the fibers were used to analyze drinking waters or deionized waters (spiked), and their analytical performance was still adequate.

3.5. Comparison with commercial fibers

The analytical performance of the obtained $\sim 3\ \mu\text{m}$ ZIF-8 based SPME fiber was compared with the most widely used SPME coatings: $85\ \mu\text{m}$ PA and $100\ \mu\text{m}$ PDMS. A comparison was carried out under optimized conditions for ZIF-8, also using an aqueous standard of $100\ \mu\text{g}\cdot\text{L}^{-1}$. Overall, the best results among commercial coatings were obtained with the PA fiber, and therefore its calibrations for the group of target analytes were also obtained (Table S3 of the ESM). Interestingly, despite the high difference in the thickness of ZIF-8 and PA (~ 28 times), the highest difference in LOD between the two fibers is only about 2.3 times (Table 1 and Table S3 of the ESM). Thus, LODs varied from $0.3\ \mu\text{g}\cdot\text{L}^{-1}$ for EHS to $0.8\ \mu\text{g}\cdot\text{L}^{-1}$ for Ace, being slightly lower than those of the ZIF-8. The aspect results clear from Figure 2, which includes a comparison of sensitivities and of the type of chromatograms obtained. Figure 2 (B) shows a normalized comparison, utilizing the normalized slope of the calibrations (slope divided by the volume of the SPME coating), taking into account that the $85\ \mu\text{m}$ PA has $\sim 0.543\ \text{mm}^3$ of coating volume and the $3\ \mu\text{m}$ ZIF-8 of $\sim 0.013\ \text{mm}^3$. The affinity of the target analytes for the ZIF-8 material is clearly evident from that comparison.

Regarding the precision, the intra-day and inter-day reproducibility of the PA fiber was determined at a concentration level of $50\ \mu\text{g}\cdot\text{L}^{-1}$. The intra-day and inter-day reproducibilities were lower than 19% and 16% respectively (Table S3 of the ESM). These results are close to those obtained with the ZIF-8 based coating at the same concentration level.

Finally, there are no differences attending to the obtained sensitivity of the commercial PA fiber as a function of the nature of the target analyte. However, the ZIF-8 fibers show certain differences between the extracted compounds.

Conclusions

The combined MOF-CVD and solvothermal approach has successfully applied in the preparation of conventional SPME fibers, taking advantage of its excellent coating thickness control and adhesion onto the fibers. The method ensures the sufficient nucleation points that yield uniform, stable, and highly reproducible coatings growth based on the MOF ZIF-8, with an estimated coating thickness of $\sim 3\ \mu\text{m}$. The fibers were able to perform in both headspace and direct immersion mode using complex wastewater

375 samples, in combination with gas chromatography – flame ionization detection, and
376 dealing with target analytes of different nature such as polycyclic aromatic hydrocarbons
377 and personal care products. The analytical performance was demonstrated, with resulting
378 inter-batch RSD values between 17-23%, lifetime values higher than 70, and limits of
379 detection down to $0.6 \mu\text{g}\cdot\text{L}^{-1}$. The analytical performance is comparable to that of
380 commercial fibers and, together with its high reproducibility and stability, supports the
381 validity of this type of coating method for the preparation of MOF-based SPME fibers.

384 **Acknowledgments**

385 P.R.-B. thank her FPI Ph.D. research contract associated with the Project Ref.
386 MAT2014-57465-R, also covering her short-term research stay at Prof. Ameloot's lab.
387 A.G.-S. thanks the Canary Agency of Research and Innovation (ACIISI), co-funded by
388 the European Social Fund, for his FPI Ph.D. fellowship. J.P. thanks the Cabildo de
389 Tenerife for his "Agustín de Betancourt" research position at ULL. V.P. thanks the
390 Spanish Ministry of Economy and Competitiveness (MINECO) for the Projects Ref.
391 MAT2014-57465-R and MAT2017-89207-R.

References

- [1] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, *Anal. Chem.* 62 (1990) 2145–2148.
- [2] N. Reyes-Garcés, E. Gionfriddo, G.A. Gómez-Ríos, M.N. Alam, E. Boyacı, B. Bojko, V. Singh, J. Grandy, J. Pawliszyn. Advances in Solid Phase Microextraction and Perspective on Future Directions. *Anal. Chem.* 90 (2018) 302–360.
- [3] É.A. Souza-Silva, E. Gionfriddo, J. Pawliszyn, A critical review of the state of the art of solid-phase microextraction of complex matrices II. Food analysis, *Trends Anal. Chem.* 71 (2015) 236–248.
- [4] É.A. Souza-Silva, R. Jiang, A. Rodríguez-Lafuente, E. Gionfriddo, J. Pawliszyn. A critical review of the state of the art of solid-phase microextraction of complex matrices I. Environmental analysis, *Trends Anal. Chem.* 71 (2015) 224–235.
- [5] É.A. Souza-Silva, N. Reyes-Garcés, G.A. Gómez-Ríos, E. Boyacı, B. Bojko, Janusz Pawliszyn, A critical review of the state of the art of solid-phase microextraction of complex matrices III. Bioanalytical and clinical applications, *Trends Anal. Chem.* 71 (2015) 249–264.
- [6] J. Xu, J. Zheng, J. Tian, F. Zhu, F. Zeng, C. Su, G. Ouyang, New materials in solid-phase microextraction, *Trends Anal. Chem.* 47 (2013) 68–83.
- [7] J. Feng, H. Qiu, X. Liu, S. Jiang, The development of solid-phase microextraction fibers with metal wires as supporting substrates, *Trends Anal. Chem.* 46 (2013) 44–59.
- [8] Y. Wen, L. Chen, J. Li, D. Liu, L. Chen, Recent advances in solid-phase sorbents for sample preparation prior to chromatographic analysis, *Trends in Analytical Chemistry* 59 (2014) 26–41.
- [9] F. Maya, J.M. Estela, V. Cerdà, Interfacing on-line solid phase extraction with monolithic column multisyringe chromatography and chemiluminescence detection: an effective tool for fast, sensitive and selective determination of thiazide diuretics, *Talanta* 80 (2010) 1333–1340.
- [10] G. Alberti, V. Amendola, M. Pesavento, R. Biesuz, Beyond the synthesis of novel solid phases: Review on modelling of sorption phenomena, *Coord. Chem. Rev.* 256 (2012) 28–45.

- 426 [11] M.O. Aziz-Zanjani, A. Mehdinia. A review on procedures for the preparation of
427 coatings for solid phase microextraction, *Microchim. Acta* 181 (2014) 1169–
428 1190.
- 429 [12] F. Meng, W. Lu, Q. Li, J.-H. Byun, Y. Oh, T.-W. Chou, Graphene-Based Fibers:
430 A Review, *Adv. Mater.* 27 (2015) 5113–5131.
- 431 [13] C. Herrero-Latorre, J. Barciela-García, S. García-Martín, R.M. Peña-Crecente,
432 Graphene and carbon nanotubes as solid phase extraction sorbents for the
433 speciation of chromium: A review, *Anal. Chim. Acta*, 1002 (2018) 1–17.
- 434 [14] I. Pacheco-Fernández, A. Gutiérrez-Serpa, A.M Afonso, V. Pino, Metallic
435 coatings in solid-phase microextraction: environmental applications. Chapter in:
436 *Advanced Ceramic and Metallic Coating and Thin Film Materials for Energy
437 and Environmental Applications*. Springer (2018) 217–243.
- 438 [15] A. Gutiérrez-Serpa, Patricia I. Napolitano-Tabares, Verónica Pino, F. Jiménez-
439 Moreno, A.I. Jiménez-Abizanda, Silver nanoparticles supported onto a stainless
440 steel wire for direct-immersion solid-phase microextraction of polycyclic
441 aromatic hydrocarbons prior to their determination by GC-FID, *Microchim.
442 Acta* 185 (2018) 341–351.
- 443 [16] I. Pacheco-Fernández, A. Gutiérrez-Serpa, P. Rocío-Bautista, V. Pino,
444 Molecularly Imprinted Polymers as Promising Sorbents in SPME Applications.
445 Chapter in: *Solid-Phase Microextraction: Advances in Research and
446 Applications*. Nova Science Publishers (2017) 147–168.
- 447 [17] M. Lasáková, P. Jandera, Molecularly imprinted polymers and their application
448 in solid phase extraction, *J. Sep. Sci.* 32 (2009) 799–812.
- 449 [18] P. Rocío-Bautista, I. Pacheco-Fernández, J. Pasán, V. Pino, Are metal-organic
450 frameworks able to provide a new generation of solid-phase microextraction
451 coatings? A review, *Anal. Chim. Acta* 939 (2016) 26–41.
- 452 [19] P. Rocío-Bautista, P. González-Hernández, I. Pacheco-Fernández, V. Pino, J.H.
453 Ayala, A.M. Afonso, Metal-organic frameworks as promising sorbents in solid-
454 phase microextraction. Chapter in: *Metal-Organic Frameworks (MOFs)
455 Chemistry, technologies and applications*. Nova Science Publishers (2016) 35–
456 54.
- 457 [20] B. Hashemi, P. Zohrabi, N. Raza, K.-H. Kim, Metal-organic frameworks as
458 advanced sorbents for the extraction and determination of pollutants from

environmental, biological, and food media, *Trends Anal. Chem.* 97 (2017) 65–82.

[21] J. Niu, Zhongyue, H. Yang, C. Ye, C. Chen, D. Li, J. Xu, L. Fan, A water resistant solid-phase microextraction fiber with high selectivity prepared by a metal organic framework with perfluorinated pores, *J. Chromatogr. A*, 1441 (2016) 16–23.

[22] Y. Wang, M. Rui, G. Lu, Recent applications of metal–organic frameworks in sample pretreatment, *J Sep Sci.* 41 (2018) 180–194.

[23] M.J. Kalmutzki, N. Hanikel, O.M. Yaghi, Secondary building units as the turning point in the development of the reticular chemistry of MOFs, *Sci. Adv.* 4 (2018) 1–16.

[24] X. Guo, S. Geng, M. Zhuo, Y. Chen, M.J. Zaworotko, P. Cheng, Z. Zhang, The utility of the template effect in metal-organic frameworks, *Coord. Chem. Rev.* 391 (2019) 44–68.

[25] O.M. Yaghi, M. O’Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Reticular synthesis and the design of new materials, *Nature* 423 (2003) 705–717.

[26] I. Taima-Mancera, P. Rocío-Bautista, J. Pasán, J.H. Ayala, C. Ruiz-Pérez, A.M. Afonso, A.B. Lago, V. Pino, Influence of Ligand Functionalization of UiO-66-Based Metal-Organic Frameworks When Used as Sorbents in Dispersive Solid-Phase Analytical Microextraction for Different Aqueous Organic Pollutants, *Molecules* 23 (2018) 2869–2882.

[27] M.H. Rosnes, F.S. Nesse, M. Opitz, P.D.C. Dietzel, Morphology control in modulated synthesis of metal-organic framework CPO-27, *Micropor. Mesopor. Mat.* 275 (2019) 207–213.

[28] P. Rocío-Bautista, V. Pino, J.H. Ayala, C. Ruiz-Pérez, O. Vallcorba, A.M. Afonso, J. Pasán, A green metal–organic framework to monitor water contaminants, *RSC Adv.* 8 (2018) 31304–31312.

[29] I. Abánades-Lázaro, R.S. Forgan, Application of zirconium MOFs in drug delivery and biomedicine, *Coord. Chem. Rev.* 380 (2019) 230–259.

[30] F. Maya, C.P. Cabello, R.M. Frizzarin, J.M. Estela, G.T. Palomino, V. Cerdà. Magnetic solid-phase extraction using metal-organic frameworks (MOFs) and their derived carbons, *Trends Anal. Chem.* 90 (2017) 142–152.

[31] X.-Y. Cui, Z.-Y. Gu, D.-Q. Jiang, Y. Li, H.-F. Wang, X.-P. Yan, In situ hydrothermal growth of metal-organic framework 199 films on stainless steel

493 fibers for solid-phase microextraction of gaseous benzene homologues. *Anal.*
 494 *Chem.* 81 (2009) 9771–9777.

495 [32] C.-T. He, J.-Y. Tian, S.-Y. Liu, G. Ouyang, J.-P. Zhang, X.-M. Chen, A porous
 496 coordination framework for highly sensitive and selective solid-phase
 497 microextraction of non-polar volatile organic compounds. *Chem Sci.* 4 (2013)
 498 351–356.

499 [33] L. Xie, S. Liu, Z. Han, R. Jiang, H. Liu, F. Zhu, F. Zheng, C. Su, G. Ouyang,
 500 Preparation and characterization of metal-organic framework MIL-101(Cr)-
 501 coated solid-phase microextraction fiber, *Anal. Chim. Acta* 853 (2015) 303–310.

502 [34] N. Zhang, C. Huang, P. Tong, Z. Feng, X. Wu, Moisture stable Ni-Zn MOF/g-
 503 C₃N₄ nanoflowers: A highly efficient adsorbent for solid-phase microextraction
 504 of PAHs, *J. Chromatogr. A* 1556 (2018) 37–46.

505 [35] G. Wang, Y. Lei, H. Song, Exploration of metal-organic framework MOF-177
 506 coated fibers for headspace solid-phase microextraction of polychlorinated
 507 biphenyls and polycyclic aromatic hydrocarbons, *Talanta* 144 (2015) 369–374.

508 [36] J. Gao, C. Huang, Y. Lin, P. Tong, L. Zhang, In situ solvothermal synthesis of
 509 metal-organic framework coated fiber for highly sensitive solid-phase
 510 microextraction of polycyclic aromatic hydrocarbons. *J. Chromatogr. A* 1436
 511 (2016) 1–8.

512 [37] G. Zhang, X. Zang, Z. Li, C. Wang, Z. Wang, Polydimethylsiloxane/metal-
 513 organic frameworks coated fiber for solid-phase microextraction of polycyclic
 514 aromatic hydrocarbons in river and lake water samples, *Talanta* 129 (2014) 600–
 515 605.

516 [38] H-B. Shang, C-X Yang, X-P Yan, Metal-organic framework UiO-66 coated
 517 stainless steel fiber for solid-phase microextraction of phenols in water samples,
 518 *J. Chromatogr. A* 1357 (2014) 165–171.

519 [39] S. Liu, Y. Zhou, J. Zheng, J. Xu, R. Jiang, Y. Shen, J. Jiang, F. Zhu, C. Su, G.
 520 Ouyang, Isorecticular bio-MOF 100–102 coated solid-phase microextraction
 521 fibers for fast and sensitive determination of organic pollutants by the pore
 522 structure dominated mechanism, *Analyst* 140 (2015) 4384–4387.

523 [40] L.D. Salmi, M.J. Heikkilä, E. Puukilainen, T. Sajavaara, D. Grosso, M. Ritala,
 524 Studies on atomic layer deposition of MOF-5 thin films, *Microporous*
 525 *Mesoporous Mater.* 182 (2013) 147–154.

- 526 [41] T. Kojima, W. Choi, M. Kawano, Single-crystal growth of coordination
527 networks via the gas phase and dependence of iodine encapsulation on the crystal
528 size, *Chem. Commun.* 50 (2014) 13793–13796.
- 529 [42] I. Stassen, N. Campagnol, J. Fransaer, P. Vereecken, D. De Vos, R. Ameloot,
530 Solvent-free synthesis of supported ZIF-8 films and patterns through
531 transformation of deposited zinc oxide precursors, *Cryst. Eng. Comm.* 15 (2013)
532 9308–9311.
- 533 [43] B.K. Keitz, C.J. Yu, J.R. Long, R. Ameloot, Lithographic deposition of patterned
534 metal–organic framework coatings using a photobase generator, *Angew. Chem.*
535 *Int. Ed.* 53 (2014) 5561–5565.
- 536 [44] I. Stassen, M. Styles, G. Greci, H. Van Gorp, W. Vanderlinden, S. De Feyter,
537 P. Falcaro, D. De Vos, P. Vereecken, R. Ameloot, Chemical vapour deposition
538 of zeolitic imidazolate framework thin films, *Nat. Mater.* 15 (2016) 304–312.
- 539 [45] I. Stassen, D. De Vos, R. Ameloot, Vapor-phase deposition and modification of
540 metal–organic frameworks: State-of-the-art and future directions, *Chem. Eur. J.*
541 22 (2016) 14452–14460.
- 542 [46] M. Krishtab, I. Stassen, T. Stassin, A.J. Cruz, O.O. Okudur, S. Armini, C.
543 Wilson, S. De Gendt, R. Ameloot, Vapor-deposited zeolitic imidazolate
544 frameworks as gap-filling ultra-low-k dielectrics, *Nat. Commun.* 10 (2019)
545 3729–3738.
- 546 [47] A.J. Cruz, I. Stassen, M. Krishtab, K. Marcoen, T. Stassin, S. Rodríguez-
547 Hermida, J. Teyssandier, S. Pletincx, R. Verbeke, V. Rubio-Giménez, S. Tatay,
548 C. Martí-Gastaldo, J. Meersschaut, P.M. Vereecken, S. De Feyter, T. Hauffman,
549 R. Ameloot, Integrated cleanroom process for the vapor-phase deposition of
550 large-area zeolitic imidazolate framework thin films, *Chem. Mater.* 31 (2019)
551 9462–9471.
- 552 [48] T. Stassin, S. Rodríguez-Hermida, B. Schrode, A.J. Cruz, F. Carraro, D.
553 Kravchenko, V. Creemers, I. Stassen, T. Hauffman, D. De Vos, P. Falcaro, R.
554 Resel, R. Ameloot, Vapour-phase deposition of oriented copper dicarboxylate
555 metal–organic framework thin films, *Chem. Commun.* 55 (2019) 10056–10180.
- 556 [49] T. Stassin, I. Stassen, N. Wauteraerts, A.J. Cruz, M. Kräuter, A.M. Coclite, D.
557 De Vos, R. Ameloot, Solvent-free powder synthesis and thin film chemical
558 vapor deposition of a zinc bipyridyl-triazolate framework, *Eur. J. Inorg. Chem.*
559 In press.

- 560 [50] H. Lan, L.D. Salmi, T. Rönkkö, J. Parshintsev, M. Jussila, K. Hartonen, M.
561 Kemell, M.-L. Riekkola, Integrated atomic layer deposition and chemical vapor
562 reaction for the preparation of metal organic framework coatings for solid-phase
563 microextraction Arrow, *Anal. Chim. Acta* 1024 (2018) 93–100.
- 564 [51] P. Rocío-Bautista, V. Pino, J.H. Ayala, A.M. Afonso, Determination of
565 Polycyclic Aromatic Hydrocarbons in Environmental Waters Using
566 Heterogeneous Magnetic Materials Based on Metal–Organic Frameworks,
567 *LCGC* 36 (2018) 464–471.
- 568 [52] N. Chang, Z.-Y. Gu, H.-F. Wang, X.-P. Yan, Metal–Organic-Framework-Based
569 Tandem Molecular Sieves as a Dual Platform for Selective Microextraction and
570 High-Resolution Gas Chromatographic Separation of n-Alkanes in Complex
571 Matrixes, *Anal. Chem.* 83 (2011) 7094–7101.
- 572 [53] D. Ge, H.K. Lee, Sonication-assisted emulsification microextraction combined
573 with vortex-assisted porous membrane-protected micro-solid-phase extraction
574 using mixed zeolitic imidazolate frameworks 8 as sorbent, *J. Chromatogr. A*,
575 1263 (2012) 1–6.
- 576 [54] D.F. Sava, M.A. Rodriguez, K.W. Chapman, P.J. Chupas, J.A. Greathouse, P.S.
577 Crozier, T.M. Nenoff, Capture of volatile iodine, a gaseous fission product, by
578 zeolitic imidazolate framework-8, *J. Am. Chem. Soc.* 133 (2011) 12398–12401.
579

Figure captions

Figure 1. Scheme of the entire procedure to obtain SPME fibers based on ZIF-8.

Figure 2. Analytical performance of the ZIF-8-based SPME fibers used in DI with GC-FID and comparison with the commercial PA fiber. A) Efficiency comparison through the slope of the calibration plot (DI-SPME-GC-FID method); B) Normalized efficiency comparison, taking into account the differences in the volumes of the coatings; C) and D) Representative chromatograms of an aqueous standard of analytes ($50 \mu\text{g}\cdot\text{L}^{-1}$) and the entire DI-SPME-GC-FID method, using the ZIF-8 and the PA fibers, respectively.

592 **Table 1.** Several quality analytical parameters of the entire DI-SPME-GC-FID method (under optimum conditions) obtained with SPME
593 coatings based on ZIF-8.

Analyte abbreviation	Working range ($\mu\text{g}\cdot\text{L}^{-1}$)	(Slope $\pm$ SD ^a) $\times 10^{-2}$	R ^b	(S _{y/x} ^c) $\times 10^{-3}$	LOD ^d ($\mu\text{g}\cdot\text{L}^{-1}$)	Intra-day RSD ^e (%)	Inter-day RSD ^f (%)	Inter-fiber RSD ^g (%)
Ace	5.0 – 70	0.96 $\pm$ 0.03	0.995	0.3	2.0	5.5	6.3	23
Fl	5.0 – 100	1.10 $\pm$ 0.03	0.995	0.3	1.8	9.8	7.7	21
EHS	2.0 – 100	5.9 $\pm$ 0.1	0.998	1.1	0.6	8.0	18	19
HMS	2.5 – 70	3.96 $\pm$ 0.08	0.998	0.5	0.8	9.3	19	19
MA	2.5 – 100	2.63 $\pm$ 0.05	0.998	0.5	1.0	15	18	17
Py	2.5 – 100	3.0 $\pm$ 0.1	0.995	0.9	1.0	16	17	18
OD-PABA	2.5 – 100	2.85 $\pm$ 0.05	0.998	0.5	1.0	16	18	18
EHMC	2.0 – 100	3.4 $\pm$ 0.1	0.996	0.9	0.8	11	18	18

^a Standard deviation of the slope for n = 7 calibration levels

^b Determination coefficient

^c Standard deviation of the residuals (or error of the estimate)

^d Limits of detection, determined as three times signal to noise ratio (3·S/N), and experimentally verified by subjecting aqueous standards at those levels to the entire DI-SPME-GC-FID method

^e Relative standard deviation, as intra-day precision (n = 4), with an aqueous standard of 50 $\mu\text{g}\cdot\text{L}^{-1}$

^f Relative standard deviation, as inter-day precision (n = 3 in each day) for 3 non-consecutive days, with an aqueous standard of 50 $\mu\text{g}\cdot\text{L}^{-1}$

^g Relative standard deviation, as inter-fiber precision (n = 3 in a day) for 3 different ZIF-8 SPME fibers, with an aqueous standard of 50 $\mu\text{g}\cdot\text{L}^{-1}$

594 **Table 2.** Representative examples from the literature, covering the use of neat MOF-based coatings in DI-SPME-GC for water analysis.
595 MOFs composites (including other materials in the SPME coatings) were not included in this comparative study.

MOF / SPME fiber thickness / thermal resistance (°C)	Analytes (number)	LOD ^a (ng·L ⁻¹)	Inter-day RSD ^b / Inter-batch RSD ^b (levels in µg·L ⁻¹)	Comparison with commercial fibers	Extraction conditions / desorption conditions / reuse cycles	Detector	Ref
UiO-66 / 7.5 µm blade / 450	OCPs ^c (2)	15 – 21	<12 (10) / non-reported	PDMS ^d /DVB ^e , PDMS ^d & PA ^f	20 min; 40 °C / 3 min; 280 °C / 80	MS ^g	[50]
MIL-53(Fe) / 2 µm arrow / 450	phenols (8)	51 – 138	<16 (50) / non-reported	PDMS ^d /DVB ^e , PDMS ^d & PA ^f	20 min; 60 °C / 3 min; 280 °C / 80	MS ^g	[50]
bioMOF-102 / 25 µm wire / 350	PAHs ^h (5) OCPs ^c (5)	0.23 – 2.3 ⁱ 0.78 – 2.2 ^j	<10 (20 ⁱ & 24 ^j ng·L ⁻¹) / non-reported	PDMS ^d /DVB ^e	35 min; RT ^k / 5 min; 260 °C / non-reported	MS ^g	[39]
ZIF-8 / 3 µm wire / 480	PAHs ^h (3) PCPs ^l (5)	0.6 – 2 µg·L ⁻¹	<19 (50) / 17 – 23 (50)	PDMS ^d & PA ^f	45 min; 35 °C / 5 min; 280 °C / 70	FID ^m	This study

^alimit of detection

^brelative standard deviation in %

^corganochlorine pesticides

^dpolydimethylsiloxane

^edivinylbenzene

^fpolyacrylate

^gmass spectrometry

^hpolycyclic aromatic hydrocarbons

ⁱfor PAHs

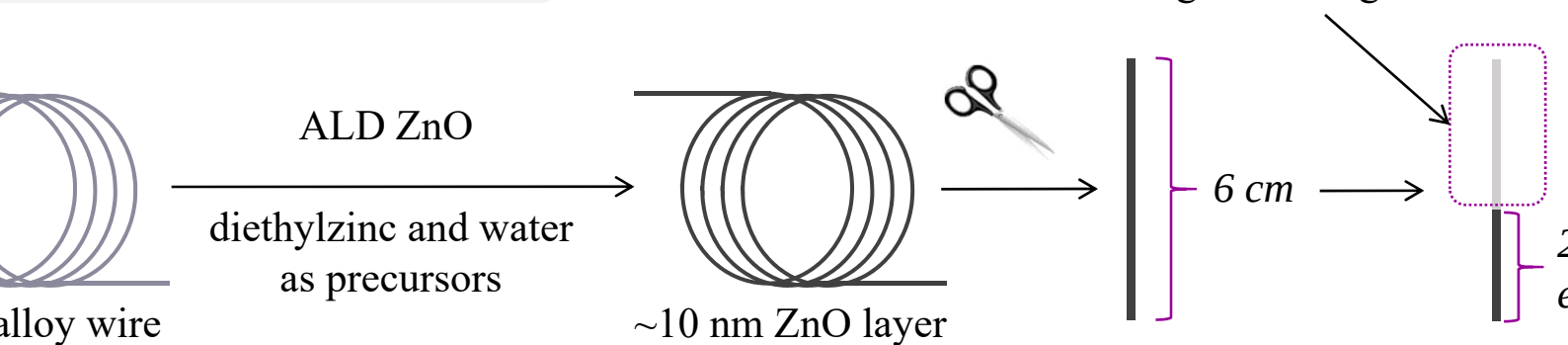
^jfor OCPs

^kroom temperature

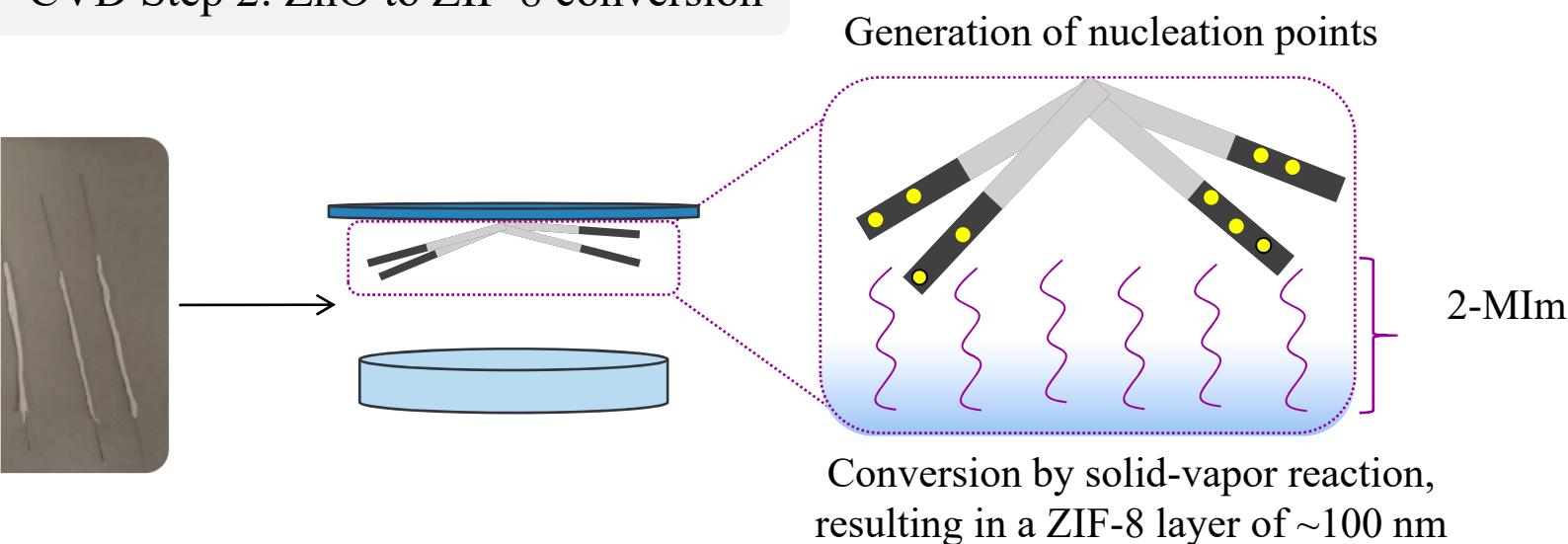
^lpersonal care products

^mflame ionization detection

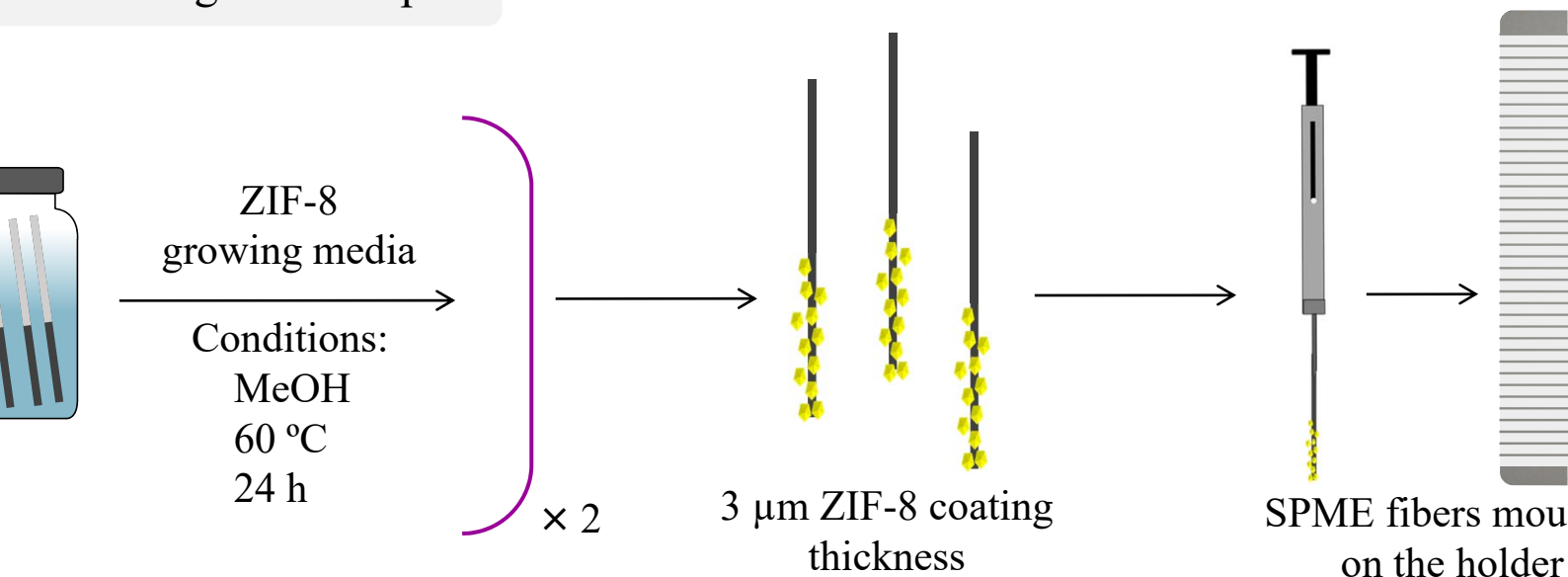
OF-CVD Step 1: ALD ZnO

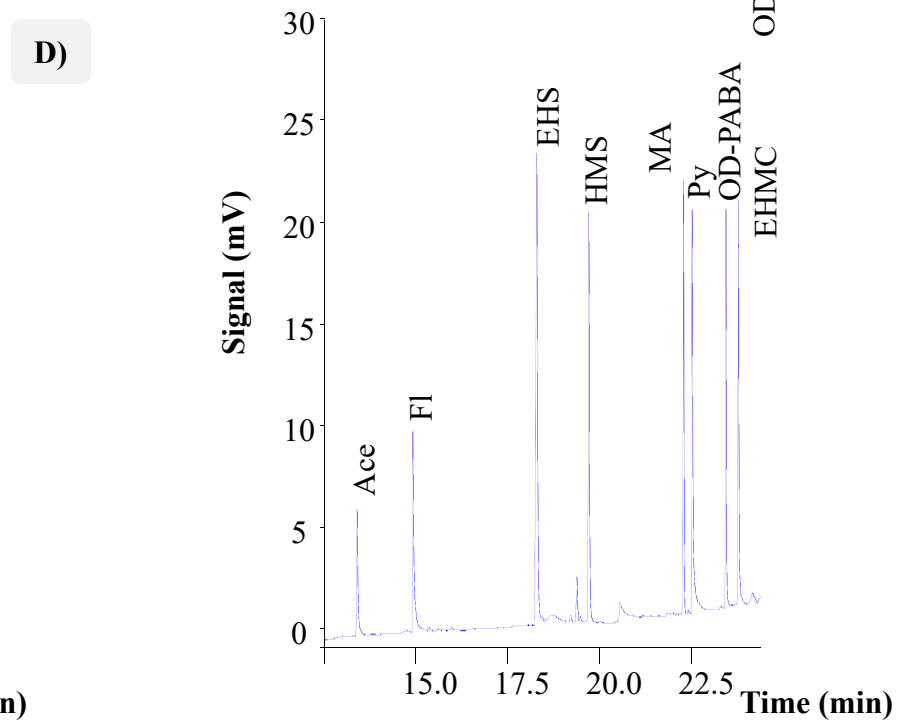
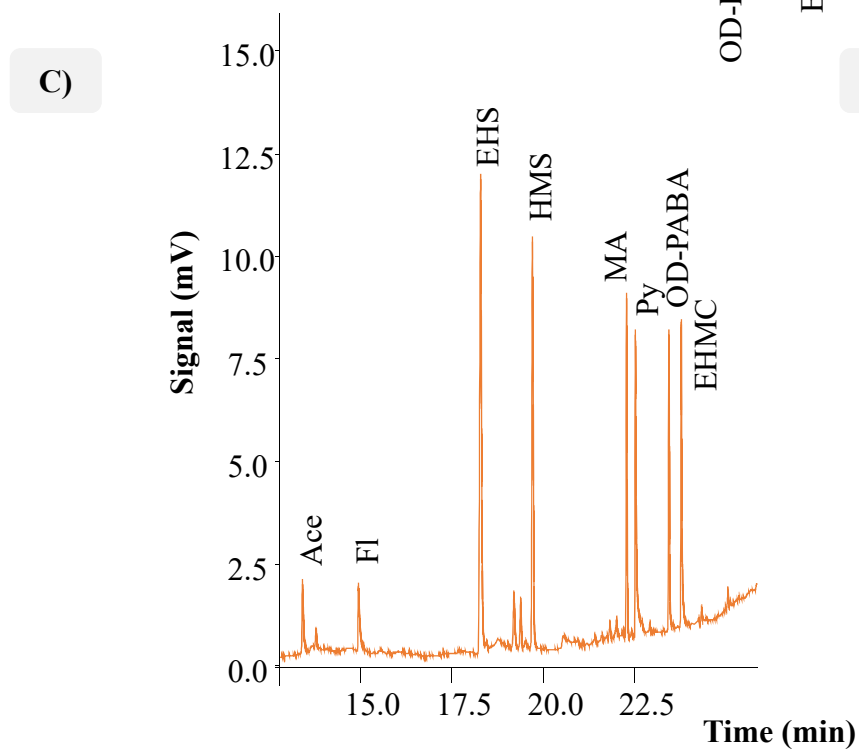
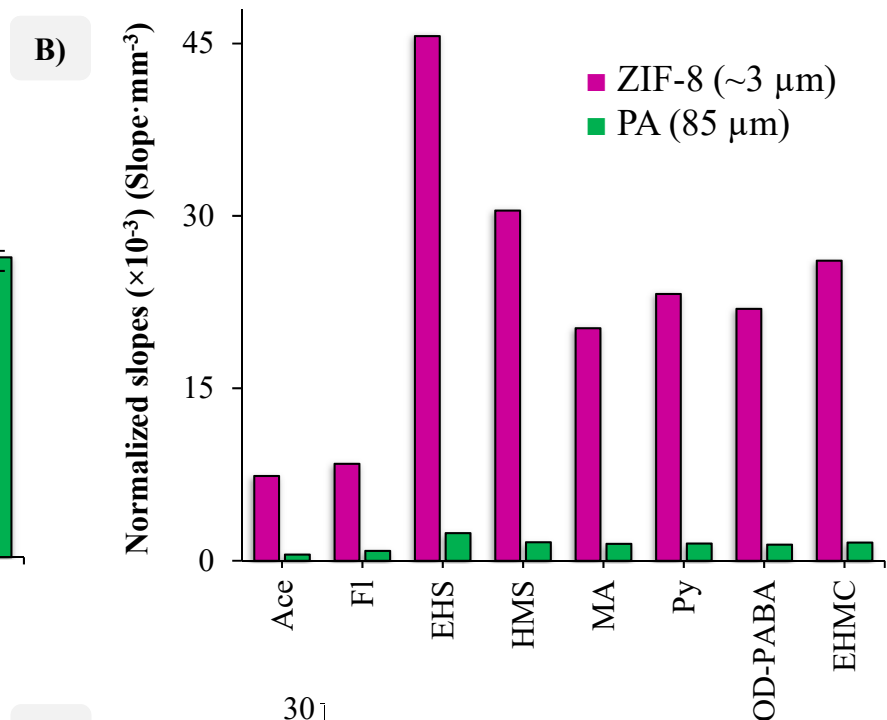
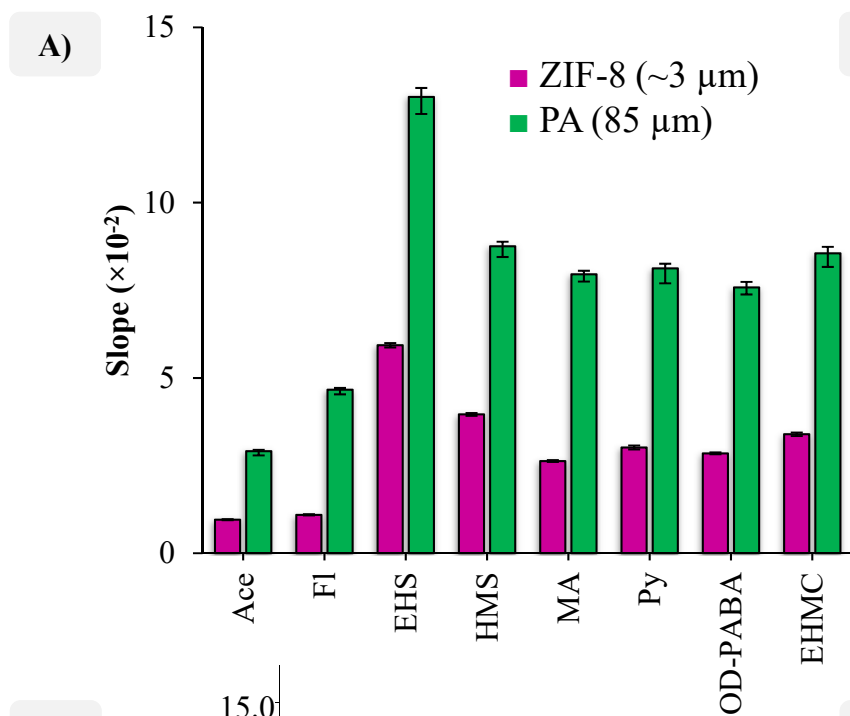


OF-CVD Step 2: ZnO to ZIF-8 conversion



Hydrothermal growth Step 3





Supplementary Material

Solid-phase microextraction coatings based on the metal-organic framework ZIF-8: ensuring stable and reusable fibers

Priscilla Rocío-Bautista¹, Adrián Gutierrez-Serpa¹, Alexander John Cruz², Rob Ameloot², Juan H. Ayala¹, Ana M. Afonso¹, Jorge Pasán³, Sabina Rodríguez-Hermida^{2*}, Verónica Pino^{1,4**}

¹*Departamento de Química, Unidad Departamental de Química Analítica, Universidad de La Laguna (ULL), La Laguna, Tenerife, 38206 Spain*

²*Centre for Membrane Separations, Adsorption, Catalysis, and Spectroscopy for Sustainable Solutions (cMACS), Department of Microbial and Molecular Systems, KU Leuven, Leuven, 3001 Belgium*

³*Departamento de Física, Laboratorio de Rayos X y Materiales Moleculares, Universidad de La Laguna (ULL), La Laguna, Tenerife, 38206 Spain*

⁴*Instituto Universitario de Enfermedades Tropicales y Salud Pública de Canarias, Universidad de La Laguna (ULL), La Laguna, Tenerife, 38206 Spain*

Table of contents

Figure S1.....	page S1
Figure S2.....	page S2
Figure S3.....	page S3
Figure S4.....	page S4
Figure S5.....	page S5
Figure S6.....	page S6
Figure S7.....	page S7
Figure S8.....	page S8
Table S1.....	page S9
Table S2.....	page S11
Table S3.....	page S12

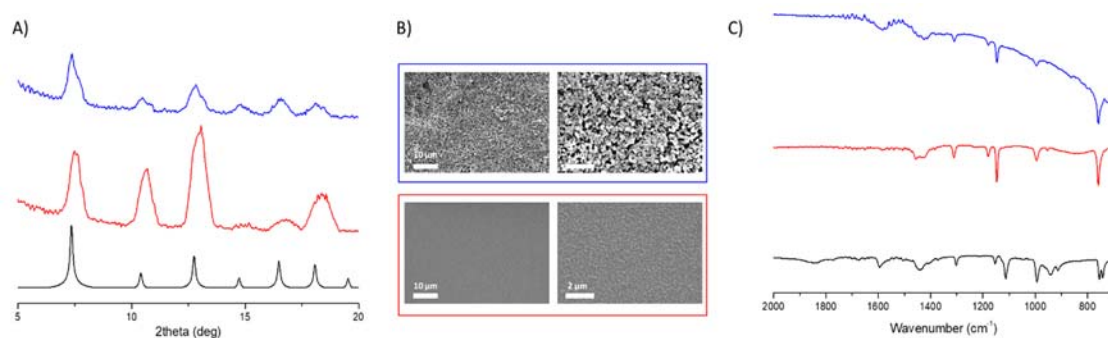


Figure S1. Characterization of the Si-witness sample. **A)** GIXRD patterns, **B)** SEM images and **C)** FTIR diagrams of the sample after the MOF-CVD method (red) and after the solvothermal step (blue). For comparison, the simulated XRD pattern and the experimental FTIR data of ZIF-8 is shown in black.

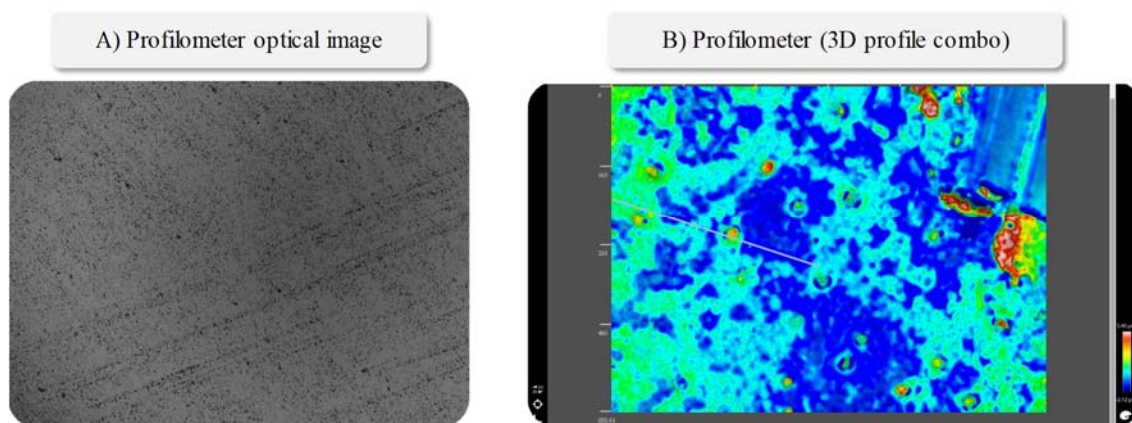


Figure S2. Surface analysis using the non-contact profilometer technique. **A)** Optical image using confocal opening. **B)** 3D combo-mode measuring the three-dimensional topography of surfaces in combination with optical calculation.

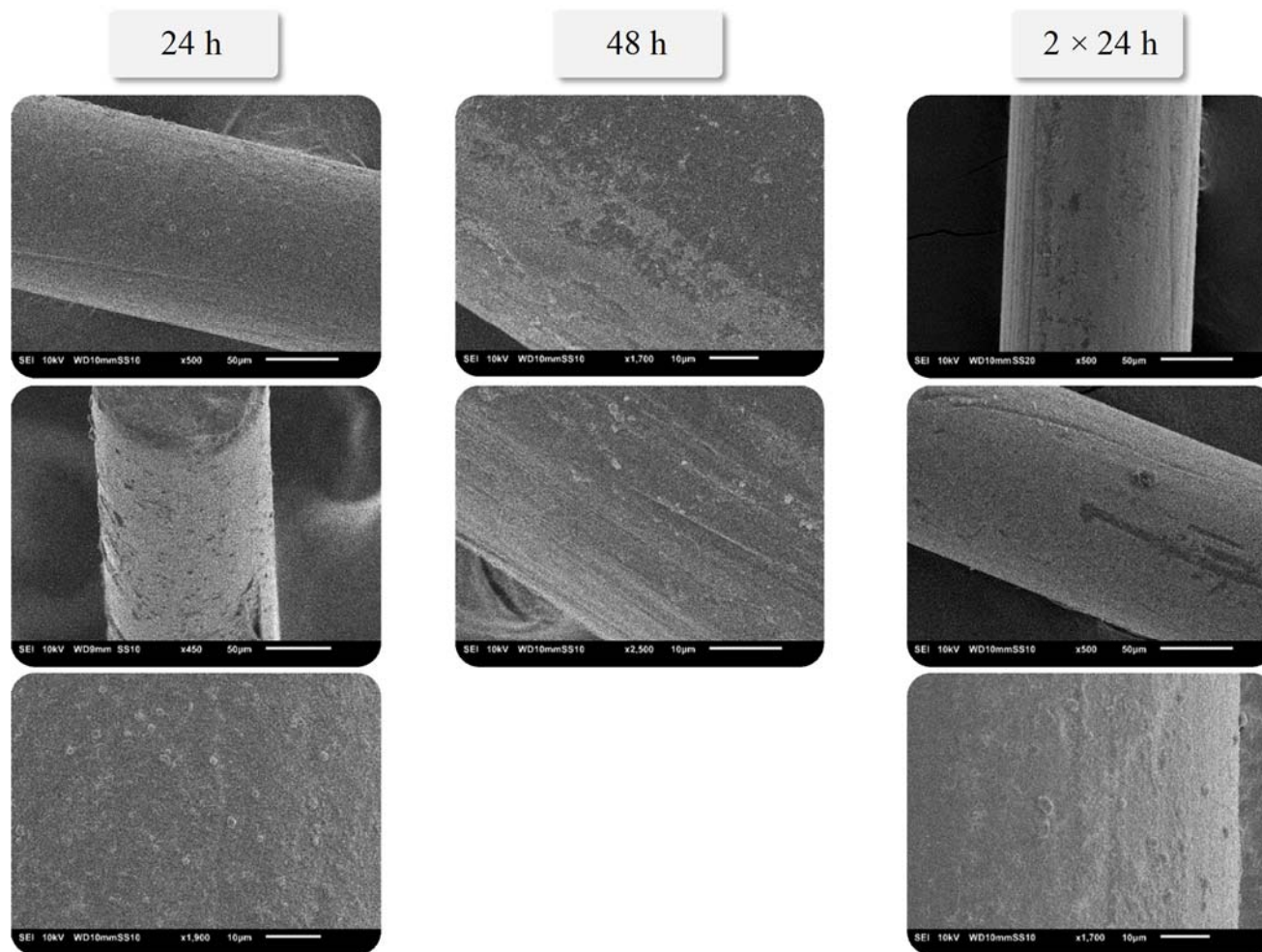


Figure S3. SEM images of SPME fibers based on ZIF-8 using different reaction times

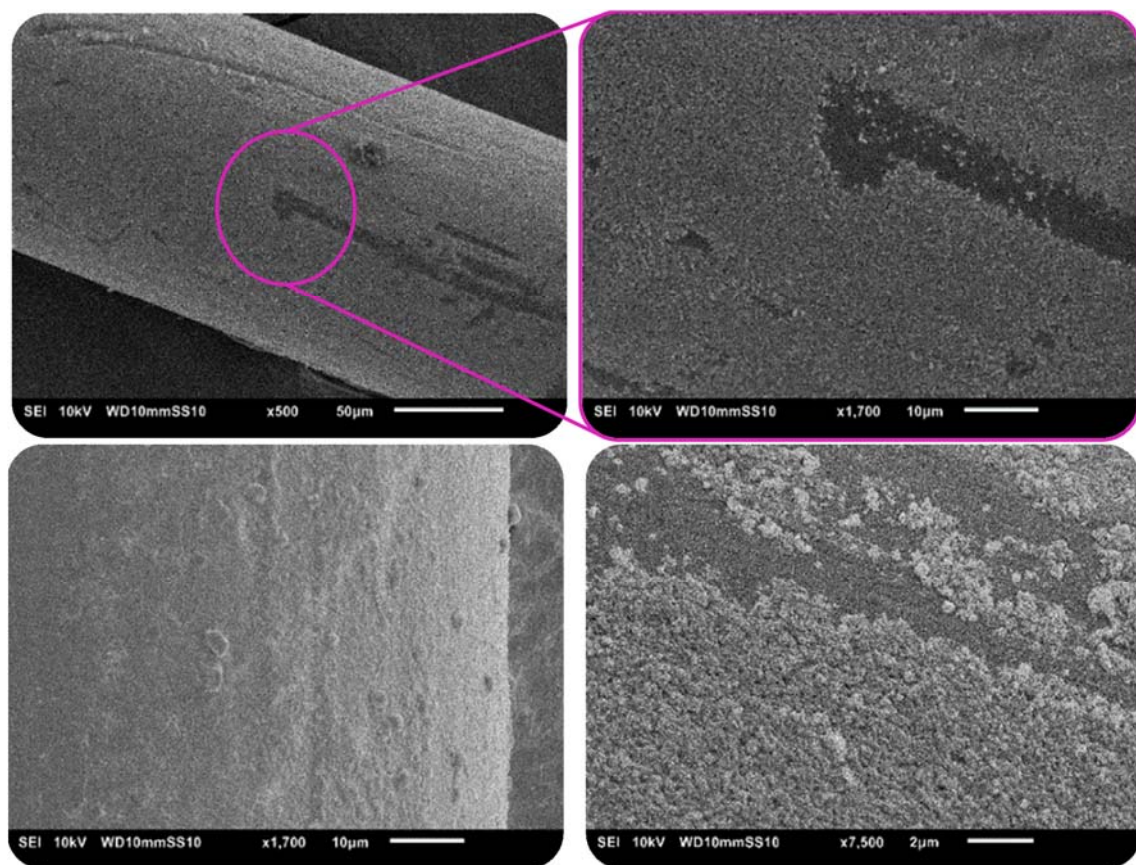


Figure S4. SEM image obtained for ZIF-8 based SPME fibers using optimum conditions.

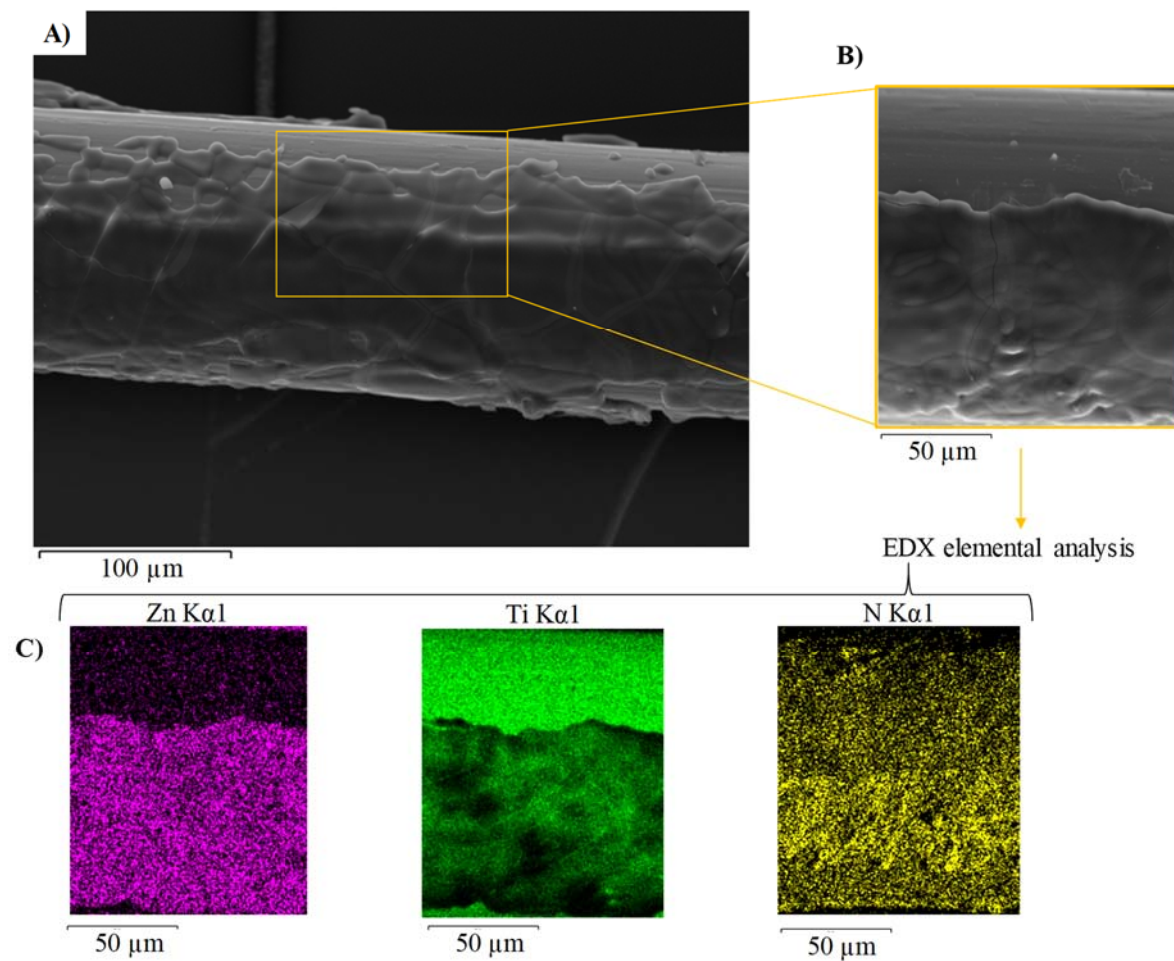


Figure S5. Characterization of the ZIF-8 SPME fiber by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX): **A)** SEM micrograph at a magnification of $\times 750$, **B)** SEM micrograph at a magnification of $\times 1560$, and **C)** EDX elemental mapping analysis showing the composition of the SPME device (coating containing Zn and support containing Ti).

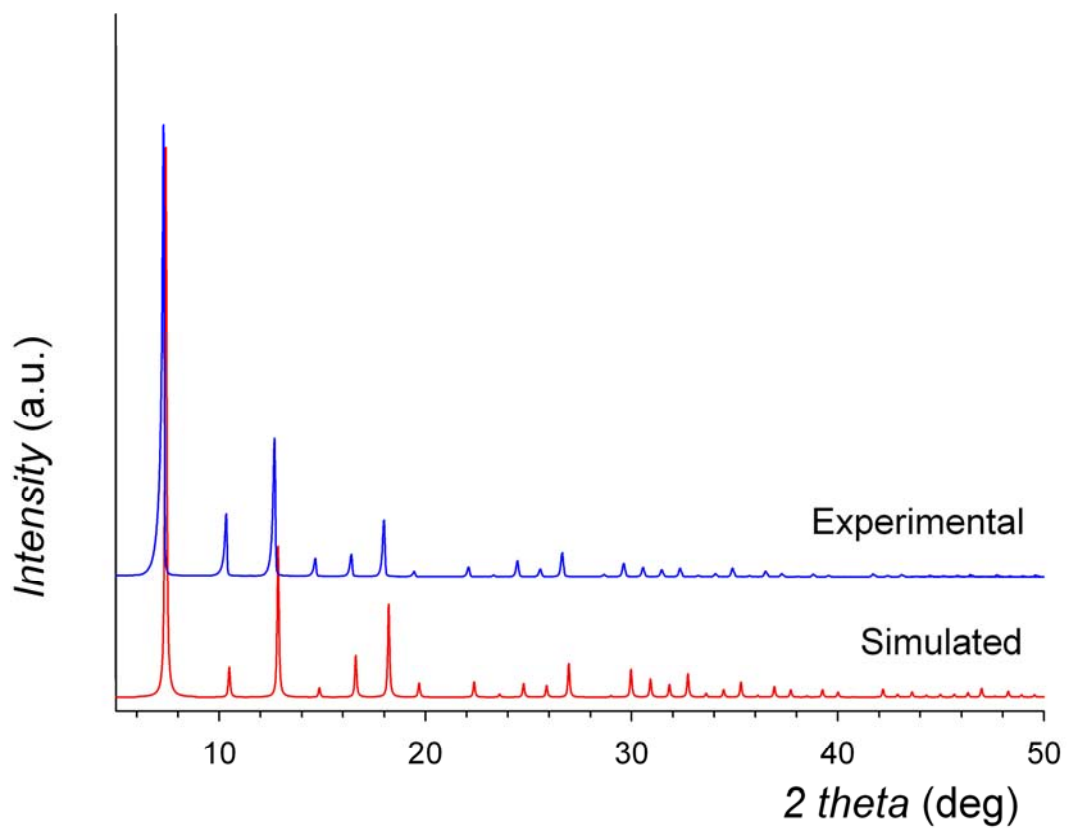


Figure S6. XRD pattern of ZIF-8 powder generated after the coating procedure compared with the simulated (CSD code for ZIF-8: 864309)

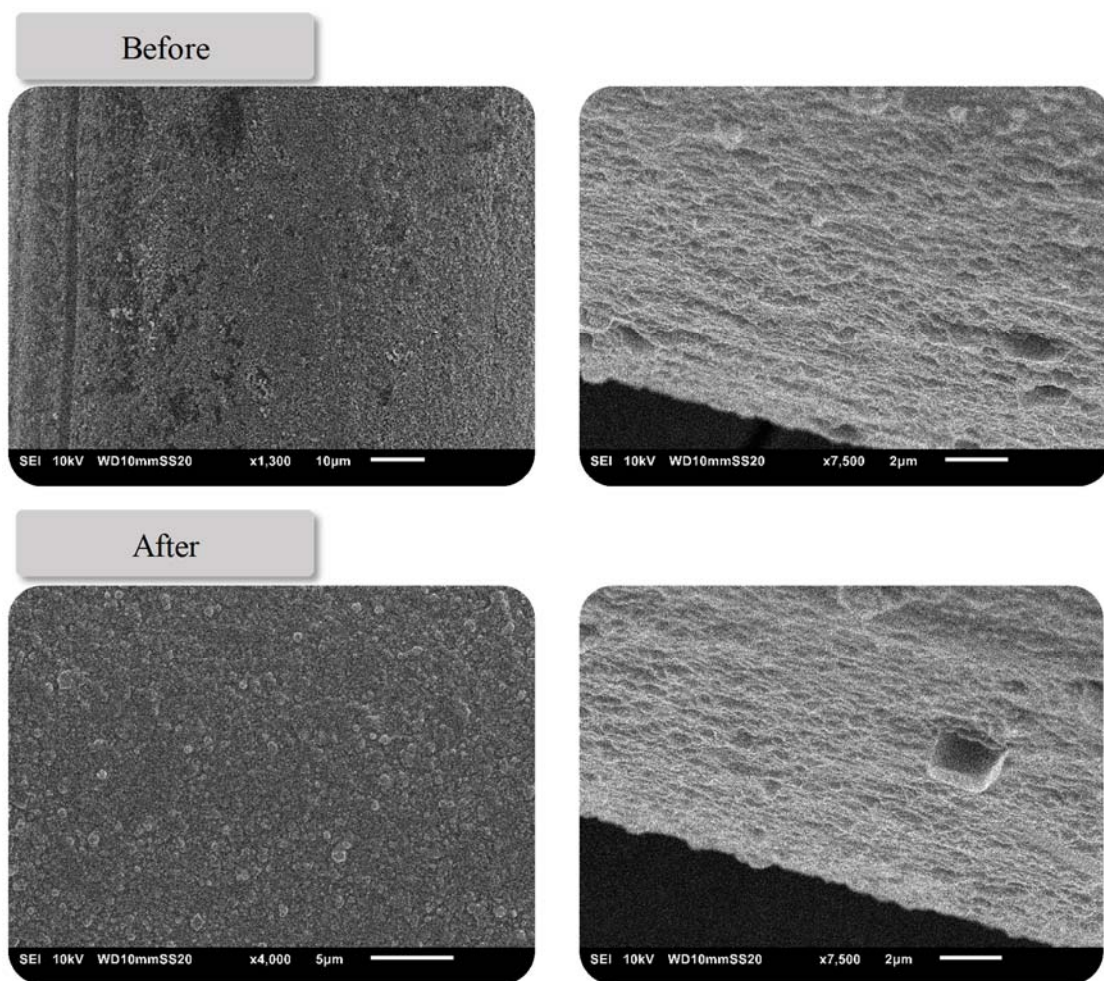


Figure S7. SEM images obtained for SPME fiber based on ZIF-8, before and after immersion of the fiber in methanol while applying ultrasounds for 5 min.

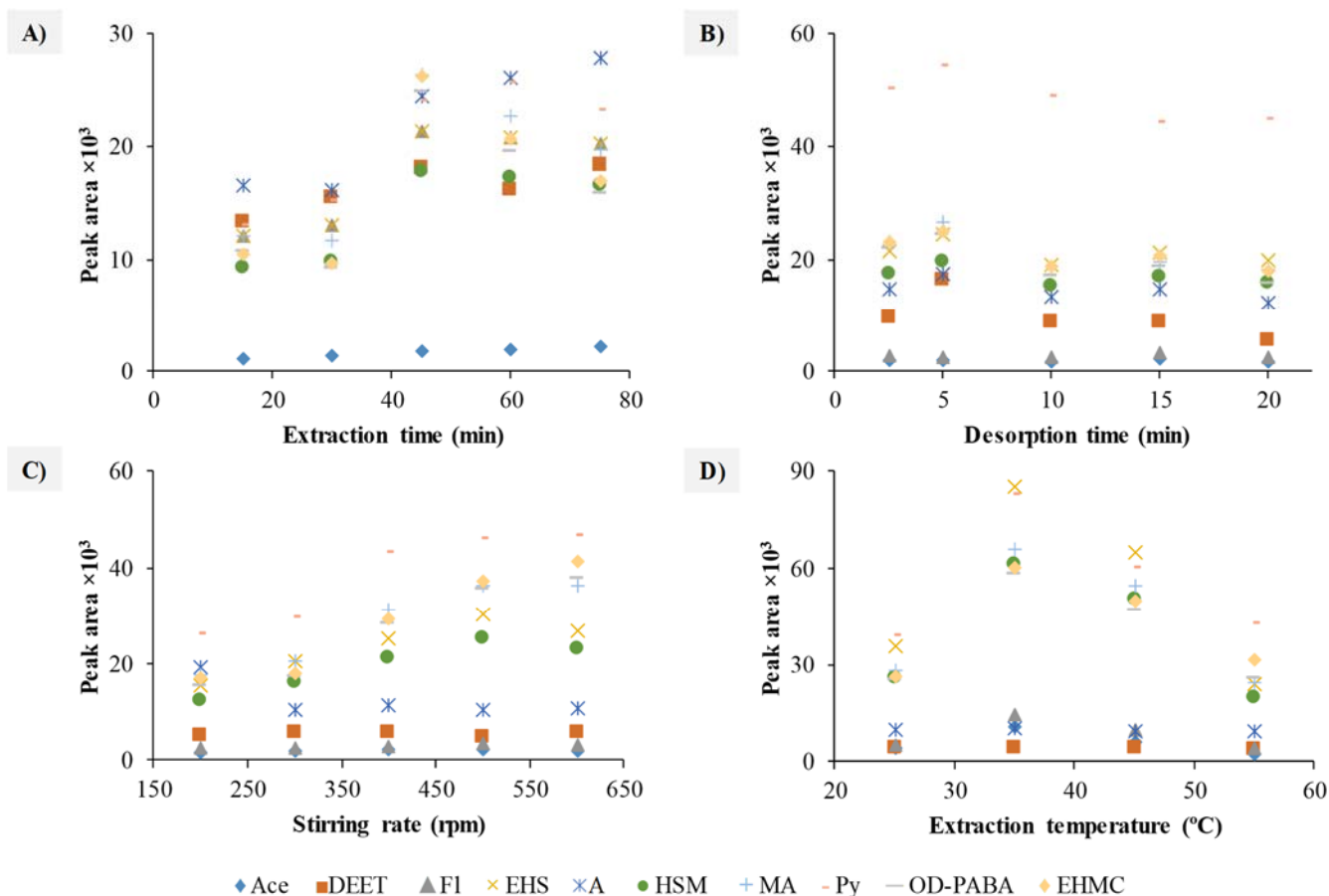


Figure S8. Optimization studies using ZIF-8 based coating as SPME fiber and GC-FID for the determination of PCPs and PAHs. **A)** Extraction time profiles were obtained using a desorption time of 5 min, stirring rate of 500 rpm, and 25 $^{\circ}\text{C}$ of extraction temperature. **B)** Desorption time profiles were obtained using an extraction time of 45 min, stirring rate of 500 rpm, and 25 $^{\circ}\text{C}$ of extraction temperature. **C)** Stirring rate profiles were obtained using an extraction time of 45 min, a desorption time of 5 min, and 25 $^{\circ}\text{C}$ of extraction temperature. **D)** Extraction temperature profiles were obtained using an extraction time of 45 min, a desorption time of 5 min, and a stirring rate of 500 rpm. Optimization in all cases was carried out using an aqueous standard containing all the analytes at 100 $\mu\text{g}\cdot\text{L}^{-1}$. Analytes abbreviations as described in Table ESM-1.

Table S1. Analytes studied by DI-SPME-GC-FID.

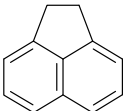
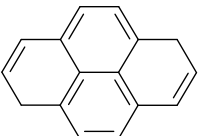
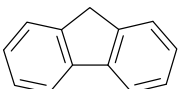
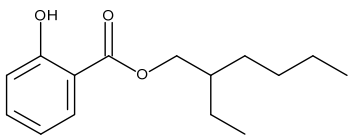
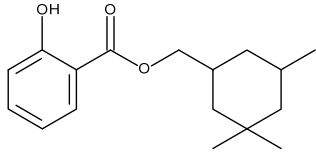
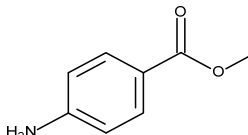
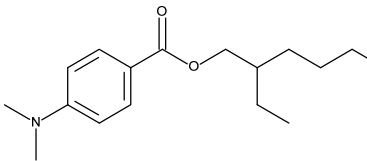
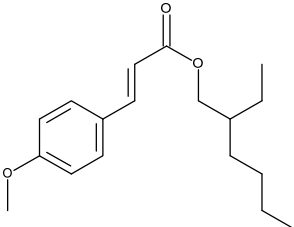
Analyte (abbreviation)	Structure	Retention time $\pm$ SD ^a	Molecular weight ^b (g·mol ⁻¹)	Volume ^c (m ³) $\times 10^{27}$	Vapor pressure ^b at 25 °C (Pa)	Log K _{ow} ^b
Acenaphthene (Ace)		13.43 $\pm$ 0.02	152.2	0.81	0.12	3.98
Pyrene (Py)		22.53 $\pm$ 0.04	202.3	1.03	5.92 $\times 10^{-5}$	4.88
Fluorene (Fl)		14.94 $\pm$ 0.03	166.2	0.86	0.08	4.18
2-Ethylhexylsalicylate (EHS)		18.30 $\pm$ 0.02	250.3	1.15	8.09	5.53
Homosalate (HMS)		19.71 $\pm$ 0.01	262.3	1.23	4.17	5.82
Methyl-anthranilate (MA)		22.27 $\pm$ 0.01	275.4	0.81	0.44	1.88

Table S1 (continued). Analytes studied by DI-SPME-GC-FID.

Analyte (abbreviation)	Structure	Retention time $\pm$ SD ^a	Molecular weight ^b (g·mol ⁻¹)	Volume ^c (m ³) $\times 10^{27}$	Vapor pressure ^b at 25 °C (Pa)	Log K _{ow} ^b
Padimate-O (OD-PABA)		23.43 $\pm$ 0.02	277.4	1.53	0.46	5.77
Ethylhexyl 4-methoxycinnamate (EHMC)		23.77 $\pm$ 0.02	290.4	1.58	0.09	6.10

^aStandard deviation of the retention times (n = 25)

^bPubChem 2019 database

^cCheméo 2019 database

Table S2. Analytical performance of the DI-SPME-GC-FID method using ZIF-8 based SPME fibers when analyzing two wastewaters sampled in Tenerife Island (Spain). Spiked content: 50 $\mu\text{g}\cdot\text{L}^{-1}$.

Analyte abbreviation	Sample 1		Sample 2	
	RR ^a	RSD ^b (%)	RR ^a	RSD ^b (%)
Ace	335 [*]	11	25.9 [*]	5.0
Fl	361 [*]	14	163.1 [*]	5.4
EHS	162 [*]	11	52.0 [*]	20
HMS	165 [*]	11	52.3 [*]	15
MA	194 [*]	21	18.7 [*]	19
Py	382 [*]	6.0	113.0	6.8
OD-PABA	187 [*]	20	36.8 [*]	18
EHMC	128	23	19.6 [*]	20

^a Relative recovery (n = 3, intra-day, spiked level = 50 $\mu\text{g}\cdot\text{L}^{-1}$)
^b Standard deviation (n = 3, intra-day)
^{*} Matrix effects present

Table S3. Several quality analytical parameters of the entire DI-SPME-GC-FID method (under optimum conditions) obtained with commercial PA SPME fiber.

Analyte abbreviation	Working range ($\mu\text{g}\cdot\text{L}^{-1}$)	(Slope $\pm$ SD ^a) $\times 10^{-2}$	R ^b	(S _{y/x} ^c) $\times 10^{-3}$	LOD ^d ($\mu\text{g}\cdot\text{L}^{-1}$)	Intra-day RSD ^e (%)	Inter-day RSD ^f (%)
Ace	2.5 – 70	2.96 $\pm$ 0.08	0.996	0.5	0.8	5.9	8.3
Fl	2.0 – 70	4.6 $\pm$ 0.1	0.998	0.6	0.6	14	9.6
EHS	1.0 – 70	13.0 $\pm$ 0.5	0.992	3.4	0.3	15	12
HMS	1.3 – 70	9.0 $\pm$ 0.3	0.996	1.7	0.4	19	15
MA	1.3 – 70	8.0 $\pm$ 0.2	0.997	1.3	0.4	15	16
Py	1.3 – 70	8.1 $\pm$ 0.3	0.995	1.8	0.4	5.4	6.7
OD-PABA	1.5 – 70	7.6 $\pm$ 0.3	0.991	2.1	0.5	8.6	16
EHMC	1.3 – 70	8.6 $\pm$ 0.3	0.991	2.4	0.4	14	16

^a Standard deviation of the slope for n = 7 calibration levels

^b Determination coefficient

^c Standard deviation of the residuals (or error of the estimate)

^d Limits of detection, determined as three times signal to noise ratio (3·S/N), and experimentally verified with aqueous standards at those level subjected to the entire DI-SPME-GC-FID method

^e Relative standard deviation, as intra-day precision (n = 4), with an aqueous standard of 50 $\mu\text{g}\cdot\text{L}^{-1}$

^f Relative standard deviation, as inter-day precision (n = 3 in each day) for 3 non-consecutive days, with an aqueous standard of 50 $\mu\text{g}\cdot\text{L}^{-1}$