

1 **Ultrasound-assisted solvent extraction of porous membrane packed solid samples: a new**  
2 **approach for extraction of target analytes from solid samples**

3 Muhammad Sajid<sup>a,\*</sup>, Mateusz Kacper Woźniak<sup>b</sup>, Justyna Płotka-Wasyłka<sup>b,\*</sup>

4 <sup>a</sup>Center for Environment and Water, Research Institute, King Fahd University of Petroleum and  
5 Minerals, Dhahran 31261, Saudi Arabia.

6 <sup>b</sup>Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology,  
7 11/12 G. Narutowicza Street, 80-233 Gdańsk, Poland.

8 \* Corresponding author

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10 Email: [msajid@kfupm.edu.sa](mailto:msajid@kfupm.edu.sa) (M Sajid)  
11 [juswasyl@pg.edu.pl](mailto:juswasyl@pg.edu.pl) (Justyna P-W)

12  
13 **Abstract**

14 For the first time, a porous membrane-based method is proposed for the extraction of target  
15 analytes directly from the solid samples. This method involves the packing of solid sample  
16 inside a porous polypropylene membrane sheet whose edges are heat-sealed to fabricate a bag.  
17 This bag is immersed in a suitable solvent and the analytes are extracted by the application of  
18 ultrasound energy. The various factors that affect the extraction performance such as extraction  
19 solvent, ultrasonication time, and ultrasound power are suitably optimized. The scope of this  
20 extraction method is very general, it can be used for the extraction of different classes of  
21 analytes from a variety of solid samples using suitable extraction solvents. The beauty of this  
22 method lies in the fact that only the small molecules such as analytes can pass through the  
23 membrane while the interfering or complex matrix species cannot pass through the membrane  
24 bag to the extraction solvent. Previously, the solid samples were first digested/dissolved into  
25 liquid medium and then analytes were extracted by membrane-protected adsorbents involving  
26 adsorption and desorption steps. With the proposed procedure, the steps of digestion/dissolution  
27 and the adsorption of analytes onto a suitable adsorbent are eliminated. Likewise, the steps of  
28 filtration, and centrifugation are not required as the solid is effectively packed inside the  
29 membrane bag. Moreover, the extraction device is low cost, portable, easy to fabricate, and  
30 simple to use in extraction process. In this work, proof of the concept is demonstrated by the  
31 extraction of polyaromatic hydrocarbons from the soil samples using GC-MS. This method  
32 provided reasonably low LODs ranging from 0.19 to 0.93 ng/mg. The inter-day precision  
33 ranged from 87.5 to 109%, while recoveries varied from  $75.1 \pm 4.9$  to  $106.0 \pm 4.5$  %.

34 **Keywords**

35 Solvent extraction; membrane-packed solid samples; microextraction; environmental analysis;  
36 sample preparation

37

38

39 **1. Introduction**

40 Despite all the major developments in analytical instrumentation, sample preparation is of  
41 critical importance in quantification of the analytes in various matrices. The need of sample  
42 preparation arises due to the demand of trace level quantification, the new regulatory  
43 obligations, and the complex matrix compositions [1]. One of the major objectives of sample  
44 preparation is to convert the sample into a form that can be introduced and analyzed by the  
45 analytical instrument. This can be accomplished by the removal of interferences,  
46 separation/preconcentration of the analytes, and (if required) conversion of the analytes into  
47 more suitable derivatives [2]. The selection of the suitable sample preparation method and  
48 related analytical instrument has great significance in analytical method development.

49 As far as the sample preparation is concerned, liquid-liquid extraction (LLE) and solid phase  
50 extraction (SPE) are two commonly used classical extraction techniques. They have advantages  
51 of better clean up and good extraction recoveries. However, both techniques consume large  
52 amounts of hazardous organic solvents and consist of multistep procedures. In addition, SPE  
53 also requires selective adsorbents for proper retention of the analytes. The synthesis of selective  
54 adsorbents involves the use of different chemicals in large quantities. In this way, both  
55 techniques are not environment friendly; also, they are time and labor extensive. As an  
56 alternative to classical LLE and SPE, the area of sample preparation is progressing toward the  
57 development of microextraction approaches that are characterized by miniaturization,  
58 simplification, and automation. Hence, the use of large amounts of organic solvents, synthetic  
59 sorbents, and the samples can be avoided. Solid phase microextraction [3], liquid phase  
60 microextraction [4], dispersive liquid-liquid microextraction [5], porous membrane protected  
61 micro-solid-phase extraction [6], and their modified versions are some examples of the widely  
62 accepted microextraction techniques.

63 Despite all the major advancements in the microextraction techniques, a kind of sample  
64 pretreatment or modification is generally required for the samples characterized by the complex  
65 matrix composition. Moreover, some of these methods cannot extract directly from the complex  
66 natured or solid samples. The cost, fragile nature of the extraction devices, and instability  
67 against certain solvents are among some major issues[7].

68 To deal with extraction of the analytes from the solid samples, the sorbent- and solvent-based  
69 microextractions generally require the digestion or dissolution of the solid samples in water or  
70 any other solvent. Further pretreatment or dilution may be needed based on the nature of the  
71 sample and selected microextraction technique. In sorbent-based techniques, two main steps  
72 are involved; first is the adsorption of the analytes from the sample onto the sorbent and second  
73 is the thermal or solvent desorption of the analytes from the sorbent.

74 Porous membrane protected micro-solid-phase extraction ( $\mu$ -SPE) was first introduced by  
75 Basheer et al., in 2006 as an alternative to multistep SPE [6]. In  $\mu$ -SPE, few milligrams of  
76 sorbent are packed inside a porous polymer membrane sheet which is heat sealed to fabricate a  
77 tea-bag like  $\mu$ -SPE device. The  $\mu$ -SPE device is then used for the adsorption of the analytes  
78 from the sample solution. The unique feature of  $\mu$ -SPE is its direct use in complex samples as  
79 sorbent is effectively protected inside the membrane bag and interfering species cannot adsorb

80 on it. That is why it has been used for a wide variety of matrices [8]. After the adsorption,  
81 analytes are back extracted into a suitable solvent.  $\mu$ -SPE has been widely used for the  
82 extraction of analytes from environmental [6,9–29], food [30–37], and biological samples [38–  
83 48].

84  $\mu$ -SPE cannot extract directly from the solid samples they need to be digested [38,41] or  
85 dissolved into a liquid [33]. In this work, we propose for the first time, a new idea for the direct  
86 extraction from the solid samples into a suitable solvent. Instead of packing the sorbent inside  
87 the porous membrane bag, we suggest packing the solid sample inside the bag. The analytes  
88 are extracted by immersing the solid sample containing bag inside the suitable solvent through  
89 the aid of the ultra-sonication. This approach eliminates the step of adsorption as analytes are  
90 directly extracted into the suitable solvent. Moreover, no sample cleanup is needed, because the  
91 interfering species cannot come out of the porous membrane. This technique results in a clear  
92 extract that can be directly injected into the analytical instrument. The proposed methodology  
93 is fast and easy to perform. In addition, no specific instrumentation is required. Depending on  
94 the solvent used, it can be considered green due to such reasons: small volume of sample as  
95 well as solvent is required, small amount of waste is produced, no much energy is consumed,  
96 depending on characteristic of analytes – several group of compounds can be extracted in single  
97 extraction. In addition, this technique can be applied for samples with complex matrices  
98 because PP membrane effectively secures the sorbent from fats, proteins and other large  
99 biomolecules. In this work, PAHs were extracted from the soil samples to demonstrate the proof  
100 of the concept. However, this idea is also extendable for variety of analytes present in various  
101 solid samples.

## 102 **2. Experimental**

### 103 **2.1. Materials and chemicals**

104 A multi-component certified standard solution (QTM PAH mix) containing 17 PAHs  
105 (Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(b)fluoranthene,  
106 Benzo(ghi)perylene, Benzo(a)pyrene, 2-Bromonaphthalene, Chrysene, Dibenz(ah)anthracene,  
107 Fluoranthene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene; listed in  
108 Table 1) at a concentrations of 2000  $\mu\text{g/mL}$  (in methylene chloride) was purchased from Sigma  
109 Aldrich (St. Louis, MO, USA). Benzo(a)anthracene-d12 was also obtained from Sigma Aldrich  
110 (St. Louis, MO, USA) and was used as internal standard (IS). HPLC-grade solvents (acetone,  
111 methanol and n-hexane) were delivered from Fisher (Loughborough, UK). Polypropylene (PP)  
112 flat membrane sheet roll (Type PP 1E (R/P), pore size: 0.1  $\mu\text{m}$ , wall thickness: 100  $\mu\text{m}$ ) was  
113 obtained from Membrana (Germany).

### 114 **2.2. Collection and preparation of soil samples**

115 The real soil samples were collected from the side of the road from the two places: village  
116 placed 50 km from Gdańsk (1-6) and city center of Gdańsk (7-13; North of Poland), while soil  
117 for method optimization and validation was collected from the place at the seaside (Gdańsk).  
118 The real samples were collected from the surface of the sandy road, and 5 cm under this point,

119 to present differences between concentration of selected PAHs in surface soil samples and in  
120 samples coming 5 cm under the surface.

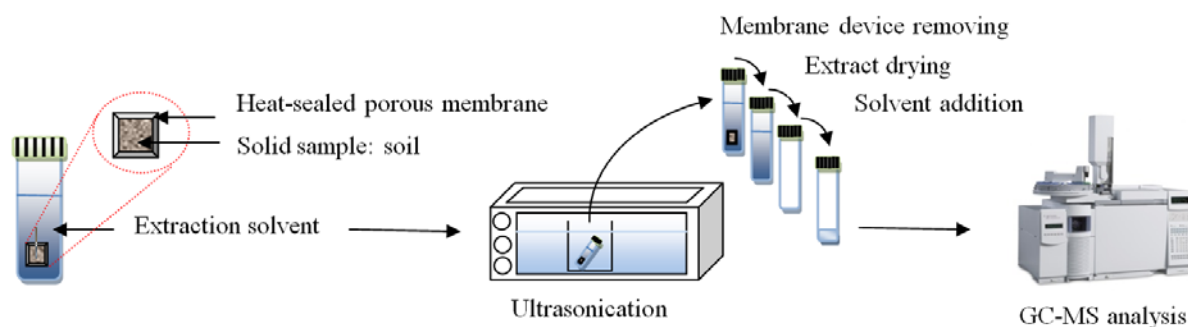
121 All samples were transported to the laboratory in glass/plastic tubes. Then, they were dried and  
122 homogenized. For optimization procedure, 25 g of soil was spiked with 1.25 mL of PAHs  
123 standard solution (stock solution: 1  $\mu\text{g}/\text{cm}^3$ ) dissolved in 20 mL of acetone. Such prepared soil  
124 was used for further optimization experiments.

### 145 2.3. Fabrication of extraction device and extraction procedure

146  
147 The membrane bag was prepared by heat-sealing the edges of porous polypropylene (PP)  
148 membrane sheet. One end was kept open for filling of solid soil samples. 2.5 mg of soil sample  
149 (spiked with 50 ng/mL of PAHs mixture standard solution or real) was filled and remaining end  
150 was heat-sealed. The dimensions of membrane device were 0.8 cm  $\times$  0.8 cm. The membrane  
151 device was placed in a 4 mL glass vial, and extraction solvent was added. Then, the vial was  
152 subjected to ultrasound bath and the extraction was allowed to take place for 25 min. The  
153 membrane device was then removed from the vial, and the extract was dried in the stream of  
154 nitrogen at 40°C. Then n-hexane (100  $\mu\text{L}$ ) was added into the vial to reconstitute the analytes.  
155 The resulting extract was then transferred to 200  $\mu\text{L}$  insert placed in autosampler vials and 2  
156  $\mu\text{L}$  aliquot was injected into GC-MS system for analysis.

157 Each optimization experiment was conducted in triplicate. The parameters that affect the  
158 efficiency of extraction including extraction solvent and its volume, extraction time, and  
159 ultrasound power were suitably optimized. Extraction efficiency was evaluated based on  
160 comparing of chromatographic peak areas.

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167 Figure 1. The workflow of the developed analytical procedure for PAHs determination in soil  
168 samples

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### 170 2.4. Preparation of stock solutions, calibrators and quality control samples

171 Stock solution of analytes was prepared in methanol by diluting the certified standard solution  
172 to reach a concentration of 10  $\mu\text{g}/\text{mL}$ . Stock solution of the IS was prepared also in methanol

173 at a concentration of 10 µg/mL. All solutions used for calibration and validation were stored at  
174 -20°C prior to analysis.

175 The calibrators ( $n=3$ ) were prepared in methanol by diluting the stock solution of analytes to  
176 concentrations of 12.5, 25, 50, 62.5, 100, 250, 500, 1000, 2500, 5000 ng/mL what correspond  
177 the concentrations of 0.5, 1, 2, 2.5, 4, 10, 20, 40, 100, 200 ng/mg of soil (these values were  
178 calculated as the mass of analytes added to the samples). The concentration of the IS in each  
179 calibrator was maintained at 500 ng/mL (20 ng/mg of soil).

180 Quality control (QC) samples were prepared in triplicate ( $n=3$ ) at two concentration levels  
181 within the range of concentrations of calibration solutions: low - 500 (LQC; 20 ng/mg soil) and  
182 high 2500 (HQC; 100 ng/mg soil) ng/mL by adding appropriate volume of stock solution of  
183 analytes and the IS to the soils samples followed by extraction procedure and GC-MS analysis.  
184 QC samples were used for the evaluation of the repeatability.

## 185 **2.5. GC-MS conditions**

186 Analyses were performed using two equipments for procedure optimization and validation:  
187 a 7890A GC System (gas chromatography; Agilent Technologies, Santa Clara, CA, USA)  
188 equipped with an electron ionization (EI) ion source and a 5975C single quadrupole mass  
189 spectrometer (MS) (Agilent Technologies) and a 7890B GC System (gas chromatograph) with  
190 an EI ion source and a 5977B single quadrupole mass spectrometer (MS) (Agilent  
191 Technologies), respectively. Both GC systems were coupled with MPS (MultiPurpose Samper)  
192 robotic autosampler and a split/splitless CIS 4 injection system (Cooled Injection System)  
193 allowing for programming temperature of injection port (Gerstel GmbH & Co. KG). This  
194 temperature was initially set at 110°C and ramped up to 270°C at 10°C/s which was held to the  
195 end of analysis. The Pulsed Splitless mode for 1 min with initial injection pressure set at 50 psi  
196 for 0.5 min was used. Subsequently, split (20:1) mode was applied. The separation of analytes  
197 was carried out on a Phenomenex ZB-5 MS capillary column (30 m × 0.25 mm id, and 0.25 µm  
198 film thickness, Shim-pol, Izabelin, Poland) with helium at a purity of 99.999% as the carrier  
199 gas in a constant flow of 1 mL/min. The oven temperature was programmed at 70°C for 1 min,  
200 then increased to 200°C at 15°C/min, next increased to 270°C at 5°C/min and finally ramped  
201 up to 300°C at 10°C/min and held for 6 min. Post-run conditioning was carried out for 2 min at  
202 300°C. The temperatures of the MS transfer line, ion source, and detector were set at 285, 230  
203 and 150°C, respectively. The MS was operated in positive mode (electron energy 70 eV). Full-  
204 scan acquisition was performed with the mass detection range set at  $m/z$  40-400 to determine  
205 retention times of analytes, optimize oven temperature gradient, and to observe characteristic  
206 mass fragments for each compound. For the identification and quantification of the analytes  
207 SIM mode was used with the ions listed in Table 1. All the ions were chosen due to their  
208 specificity and abundance. Data acquisition and analysis were accomplished by MassHunter  
209 GC/MS Acquisition software by Agilent Technologies (version B.07.05.2479) and Maestro 1  
210 software by Gerstel GmbH & Co. KG (version 1.5.3.2/3.5). The optimization and validation  
211 was performed on two different instruments due to which difference in peak intensities was  
212 observed.

213 Table 1. Provides information on retention time and quantitative ion of analytes used for  
214 detection.

## 215 **2.6. Method validation**

216 The new developed membrane supported GC-MS-based method for PAHs' quantification was  
217 validated according to international guidelines in the field of our study [cyt.] in terms of:  
218 selectivity, linearity, sensitivity - limit of detection (LOD) and limit of quantification (LOQ),  
219 matrix effect, carry-over effect, recovery and repeatability.

220 The selectivity experiments were performed to verify the presence of endogenous or exogenous  
221 compounds in the retention times of the analytes and the IS. For this purpose, 6 various origin  
222 soil blank samples were analysed after the extraction step according to procedure described in  
223 section 2.3.

224 To compensate the variability of the detector signal during different analyses and losses of  
225 analyte in the extraction step (to increase repeatability), the internal standard calibration was  
226 performed. In order to increase the accuracy of the method, the weighted linear regression was  
227 applied to the calibration curves. The linearity of the weighted calibration curves were  
228 expressed as the correlation coefficient ( $r$ ). The LOD and LOQ were assessed based on  
229 regression parameters of weighted calibration curves and calculated using the following  
230 formula:  $LOD=3.3 \cdot S_b/a$ , where  $S_b$  is the standard deviation of the intercept and  $a$  is the slope of  
231 the calibration curve. The values of limit of quantitation (LOQ) were calculated as three times  
232 LOD.

233 The matrix effects (ME) of the developed method was evaluated using procedure described by  
234 Matuszewski *et al.* [49]. ME were investigated at two concentration levels, similar to QC  
235 samples 500 and 2500 ng/mL and was calculated by comparing the responses (peak area of  
236 each analyte against peak area of the IS) for appropriate solution of analytes prepared in  
237 methanol (sets A,  $n=3$ ) with those measured in blank soil extracts spiked after extraction  
238 procedure with the same analyte amount (sets B,  $n=3$ ). The following formula was used  
239  $ME[\%]=B/A*100\%$ .

240 The potential for carry-over of the analyte and the IS to the subsequent sample in the  
241 autosampler batch was evaluated by injecting 2  $\mu$ L of methanol after calibration solution at the  
242 highest concentration level from the calibration curve (5000 ng/mL). The test was performed  
243 in six replicates.

244 The recoveries (in %) of the developed method were evaluated by comparing the analyte-to-IS  
245 peak area ratios of the spiked and extracted blank soil samples with the corresponding peak area  
246 ratios of the matrix extracts fortified with standards at concentrations of QC samples ( $n=3$ ). In  
247 this test the IS was added after extraction as was suggested by Matuszewski *et al.* [49]. The  
248 repeatability of the method was determined as intra- and inter-assay accuracy and precision.  
249 Intra-day assay measurements were carried out by analysing QC samples ( $n=3$ ). To determine  
250 the inter-day assay repeatability the tests were repeated over three different days. The accuracy  
251 (A%) of the method was calculated using following formula:  $A=c_m/c_{nom} * 100\%$  ( $c_m$  is the



252 measured concentration of analytes in QC samples and  $c_{nom}$  is the appropriate nominal  
253 concentration). Precision was assessed as correlation coefficients (CVs) of above-mentioned  
254 measurements.

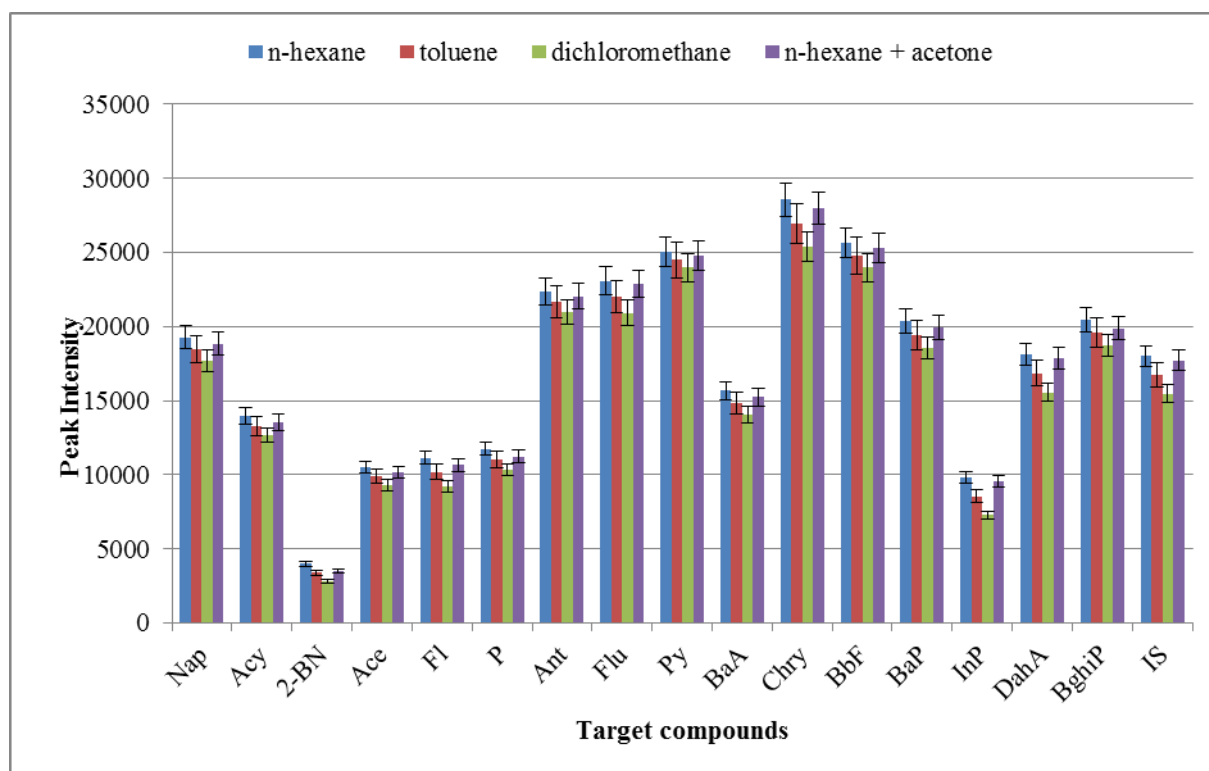
### 255 3. Results and discussion

#### 256 3.1. Optimization of extraction procedure

257 Several parameters affect the extraction efficiency including extraction solvent and its volume,  
258 extraction time and ultrasound power. Thus, these parameters were examined during this  
259 experiment.

##### 260 3.1.1. Extraction solvent

261 The extraction solvent should be carefully selected as it has significant importance in extraction  
262 process. Affinity between extraction solvent and analytes in terms of polarity is an important  
263 parameter to consider. One mixture of organic solvents (acetone: n-hexane, 1:1 v/v) and three  
264 organic solvents and with varying polarity index (n-hexane, dichloromethane and toluene) were  
265 employed as extraction solvent. N-hexane was found the most effective compared to other  
266 examined solvents and it was selected as an optimum extraction solvent (Fig. 2). PAHs were  
267 effectively extracted into n-hexane due to non-polar nature of both the PAHs and solvent.



268  
269 Figure 2. Selection of extraction solvent based on peak intensity for the determination of PAHs  
270 with ultrasound-assisted solvent extraction of porous membrane packed solid samples.

271 To elute the target compounds from porous membrane packed solid samples in a reproducible  
272 manner, the volume of extraction solvent should be sufficient enough to completely immerse

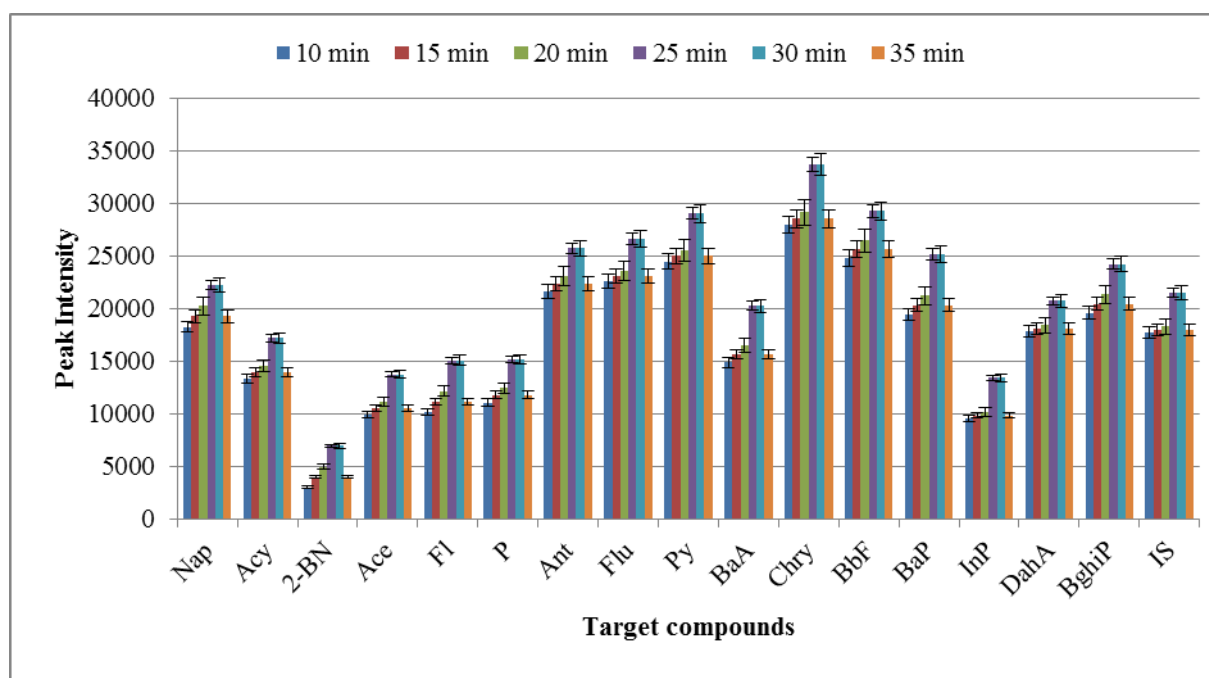
273 the membrane device. In these experiments, we selected a constant volume of solvent as  
274 1 mL, which was enough to completely immerse the solid sample containing membrane bag.  
275 After the completion of the extraction, the solvent was evaporated to dryness and reconstituted  
276 in 100 $\mu$ L of n-hexane.

277

### 278 3.1.2. Time of extraction (ultra-sonication)

279 Since proposed here procedure is time dependent, the mass transfer of analytes increases with  
280 extraction time until an equilibrium or steady state is attained. Thus, the time of extraction was  
281 examined in the range of 10–35 min. After 25 min, no further increase in peak areas of analytes  
282 was observed till 35 min. However, some decrease was observed. This attributed to rise of  
283 temperature by longer sonication times, which may evaporate analytes to the headspace and  
284 they can escape upon opening the vial. The longer times may also cause degradation of analytes.

285 Hence, extraction time of 25 min was selected as optimum extraction time (Figure 3).



286

287 Figure 3. Selection of the extraction time based on peak intensity for the determination of PAHs  
288 with ultrasound-assisted solvent extraction of porous membrane packed solid samples.

### 289 3.1.3. Ultrasound power

290 Because the extraction process was supported by ultra-sonication, ultrasound power was  
291 evaluated in the range of 10 W – 100 W. Peak areas were increased up to 60 W and then became  
292 constant. However, after the application of 80W and higher powers, a significant decrease in  
293 the peak areas of the analytes were observed. It can be attributed to the fact that higher  
294 ultrasound power can increase temperature, which may result in evaporation of analytes in  
295 headspace over the vial. The second reason can be speculated as degradation of analytes under



296 intensive sonication for longer times. Hence, 60 W was selected as an optimum ultrasound  
297 power.

### 298 **3.2. Method validation**

299 The developed GC-MS-based method includes three ions (1 quantifier and 2 qualifiers). An  
300 example chromatogram in SIM mode of all analytes at a concentrations of 1000 ng/mL and the  
301 IS (500 ng/mL) is presented in Fig. 4a. The increased sensitivity, better peak shape, and the  
302 better SNR was enabled by careful optimization of chromatographic conditions, such as the  
303 temperature of the injector, the initial and final column temperature, the temperature rate and  
304 carrier gas flow, as well as the injection mode (split, splitless by different period of the time,  
305 and pulsed splitless using various pressure conditions maintained by different time).

306 No interfering peaks of additional naturally occurring substances in soil in retention times of  
307 analytes and the IS which could have obstruct the quantification were reported in the soil blank  
308 samples investigated for selectivity (Fig. 4b). Therefore, the presented method can be  
309 considered as specific and selective for the determination of PAH in soil samples. No  
310 significance MEs were observed for most analytes, because there were determined in the range  
311 of 89.8-111. Such MEs varied between 80-120% can be perceived as soft and can be neglected  
312 [50]. Only for Chrysene there was observed high enhancement of the detector signal while was  
313 injected in matrix extract compared to the signal injected in the solvent (ME=160-188%).  
314 Therefore, to avoid necessity of preparation matrix-match calibration solutions for calibration,  
315 this compound was not used for further analysis. A carry-over effect was not observed. Seven-  
316 or six-point calibration curves were constructed using the peak area ratio (analytes vs IS) plotted  
317 against the concentration (number of replicates for each level  $n=3$ ). The method was shown to  
318 be linear within the tested calibration ranges. The details on curves' range for each analyte and  
319 corresponding weighting factors are shown in Table 2. The data of correlation coefficients ( $r$ )  
320 of the weighted calibration curves, their regression parameters and LODs and LOQs for each  
321 analyte are presented also in Table 2. The accuracy, precision, recoveries data for intra- and  
322 inter-day measurements, and MEs values are summarized in Table 3. Importantly, for three  
323 compounds (Fluorene, Benzo(a)pyrene, and Indeno(1,2,3-cd)pyrene) the recoveries were  
324 below 80%, and therefore, there were took into account to calculate accuracy and precision.

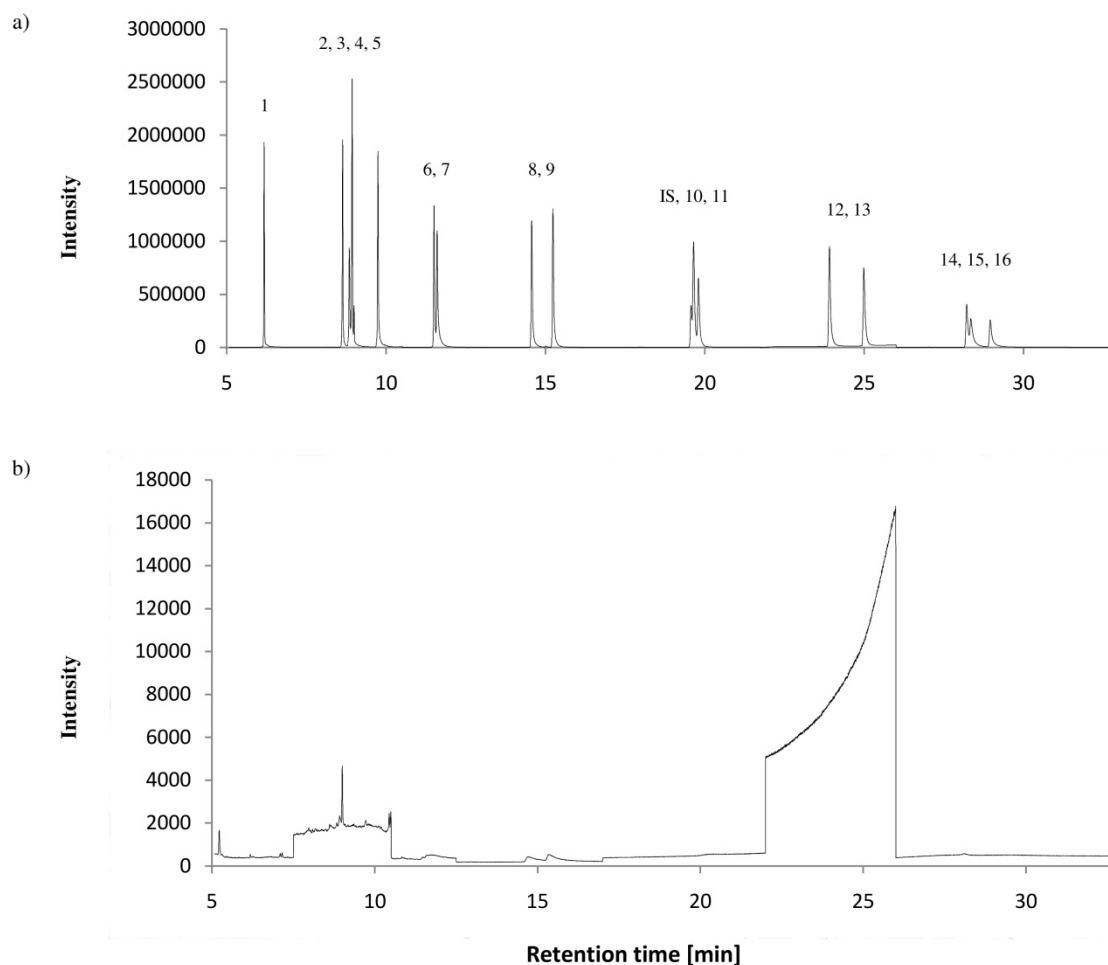
325 Based on the obtained validation parameters which fulfil the established international criteria  
326 for analytical methods, it could be stated, that the presented method for the quantification of  
327 PAH in soil samples is characterized by high accuracy and precision and can be used for the  
328 analysis of real samples.

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335 Fig. 4 GC-EI-MS chromatogram of a) mixture of PAH (1000 ng/mL) and the IS (500 ng/mL)  
 336 in SIM mode, b) blank soil sample in SIM mode for selectivity test (numbers correspond  
 337 compounds listed in Table 1).

### 338 3.3. Analysis of real samples

339 The proposed method was carried out to determine the PAHs levels in the real soil samples.  
 340 Each measurement was performed four times. The information on concentration levels for  
 341 PAHs determined in real samples are presented in Table 4. All of the compounds were  
 342 determined in each sample. It was found that soil samples coming from village contain lower  
 343 concentrations of PAHs than those coming from city center. In addition, in most cases, samples  
 344 collected 5 cm under surface are characterized by lower concentration level of PAHs than those  
 345 collected from the surface of the road. This was expected as in soils from large cities, along  
 346 transport routes, in the vicinity of industrial plants, the level of these pollutants can be very  
 347 high. It was expected that in village, some samples will be free of PAHs but this not happened.  
 348 This can be because the village is placed close to Tricity (a metropolitan area in Poland  
 349 consisting of three cities in Pomerania: Gdańsk, Gdynia and Sopot, as well as minor towns in  
 350 their vicinity). And as it is well known, the transport of pollutants in the atmosphere poses a

351 danger that in areas of limited anthropopressure - with minimal sources of pollution - their level  
352 can be significant.

353

#### 360 **4. Conclusion**

361 For the first time, a simple and cost-effective method is proposed for the extraction of the target  
362 analytes from the solid samples. This method is based on packing of the solid sample inside a  
363 porous membrane bag which is subjected to solvent extraction under ultrasonication. This  
364 method eliminates many steps associated with conventional sorbent-based membrane  
365 extraction. The steps like sample pretreatment, digestion/dissolution, and adsorption of analytes  
366 on a selective adsorbent are omitted. In addition, it does not require special equipment for  
367 filtration and centrifugation. This method has shown excellent analytical figures of merit for  
368 the extraction of PAHs in soil samples. In comparison with conventional methods of PAHs  
369 determination presented in the literature [51, 52, 53], this method present lower LOD and LOQ,  
370 thus allow to determine ultra-trace concentration level of PAHs. In addition, it is faster and do  
371 not requires any additional instrumentation. The applications of this method can be further  
372 extended to other analytes present in variety of solid matrices. This work represents mainly a  
373 proof of concept, we expect some interesting applications of this method in the future.

#### 374 **Acknowledgement**

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376 Institute, at King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

#### 377 **Authors' contribution**

378 The idea of this work was proposed by Muhammad Sajid who also suggested the experimental  
379 design and contributed in manuscript preparation mainly in write up of the abstract,  
380 introduction, and conclusion and formatting of the rest of the manuscript. Mateusz K. Woźniak  
381 and Justyna Płotka-Wasyłka performed collection of samples, experimentation, data analysis,  
382 and write up of experimental as well as results and discussion part.

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599 **Table 1.** List of target analytes, their retention times, and selected ions for SIM mode

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L.p.	Detection window (time range [min])	Compound	Rt [min]	Quantitative ion	Qualitative ions
1	1 (5-7,5)	Naphthalene	6.13	128	127, 129
2	2 (7,5-10,5)	Acenaphthylene	8.65	152	151, 153
3		2-Bromonaphthalene	8.85	206	127, 208
4		Acenaphthene	8.95	153	154, 152
5		Fluorene	9.76	166	165, 167
6	3 (10,5-12,5)	Phenanthrene	11.52	178	176, 179
7		Anthracene	11.61	178	176, 179
8	4 (12,5-17)	Fluoranthene	14.59	202	200, 203
9		Pyrene	15.26	202	200, 203
10	5 (17-22)	Benzo(a)anthracene	19.67	228	226, 229
11		Chrysene	19.83	228	226, 229
12	6 (22-26)	Benzo(b)fluoranthene	23.94	252	250, 253
13		Benzo(a)pyrene	25.01	252	250, 253
14	7 (26-)	Indeno(1,2,3-cd)pyrene	28.24	276	277, 274
15		Dibenz(ah)anthracene	28.36	278	276, 279
16		Benzo(ghi)perylene	28.99	276	277, 274
18	5	IS	19.6	240	236, 120

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**Table 2** Quantification and calibration data for PAH analysed in this study

Analyte	Calibration range [ng/mg]	r	LOD [ng/mg]	LOQ [ng/mg]
Naphthalene	1 - 200	0.9995	0.32	0.97
Acenaphthylene	0.5 - 200	0.9993	0.19	0.57
2-Bromonaphthalene	1 - 200	0.9994	0.38	1.1
Acenaphthene	1- 200	0.9995	0.27	0.8
Fluorene	1.5 - 200	0.9992	0.53	1.6
Phenanthrene	1 - 200	0.9991	0.31	0.94
Anthracene	1.5 - 200	0.9994	0.51	1.5
Fluoranthene	2 - 200	0.9990	0.60	1.8
Pyrene	0.5 - 200	0.9992	0.25	0.77
Benzo(a)anthracene	1 - 200	0.9996	0.34	1.0
Benzo(b)fluoranthene	2 - 200	0.9995	0.63	1.9
Benzo(a)pyrene	1.5 - 200	0.9996	0.46	1.4
Indeno(1,2,3-cd)pyrene	2.5 - 200	0.9987	0.83	2.5
Dibenzo(ah)anthracene	2.5 - 200	0.9993	0.93	2.8
Benzo(ghi)perylene	2.5 - 200	0.9995	0.89	2.7

*r* - Correlation coefficient, *LOD* - limit of detection, *LOQ* - limit of quantification

632 **Table 3 Summary of the validation study: accuracy (precision), recoveries±SD [%], and ME [%] (n=3)**

Analytes	C	Intra-day			Inter-day	Recovery	ME [%]
		Day1	Day 2	Day3			
Naphthalene	20	100 (5.2)	94.7 (3.0)	93.9 (3.6)	96.2 (3.4)	97.2 ± 1.6	97.5
	100	103 (1.7)	101 (1.4)	96.8 (1.6)	100 (3.2)	91 ± 2.2	96.5
Acenaphthylene	20	95.4 (7.5)	101 (3.9)	100 (4.8)	98.8 (3.0)	90.9 ± 1.7	99.8
	100	102 (1.3)	104 (1.8)	97.5 (4.1)	101 (3.3)	97.8 ± 2.3	102
2-Bromonaphthalene	20	96.4 (5.5)	92.1 (3.8)	98.2 (4.2)	95.6 (3.3)	100 ± 3.6	104
	100	104 (1.7)	101 (0.4)	99.1 (3.8)	101 (2.4)	98.6 ± 2.9	96.1
Acenaphthene	20	97.8 (7.3)	94.2 (3.5)	101 (6.1)	97.7 (3.5)	101 ± 3.8	101
	100	104 (1.5)	101 (1.4)	95.2 (4.5)	101 (4.5)	93.7 ± 4.2	98.8
Fluorene	20	96.4 (6.5)	93.1 (3.5)	102 (5.1)	97.2 (4.6)	77.5 ± 3.9	107
	100	107 (1.4)	100 (2.8)	97.8 (3.7)	102 (4.7)	78.6 ± 2.6	100
Phenanthrene	20	93.5 (4.9)	98.1 (6.4)	99.5 (5.1)	97.2 (3.2)	89.9 ± 5.7	109
	100	101 (1.8)	105 (2.6)	95.2 (3.5)	103 (2.7)	99.1 ± 1.2	108
Anthracene	20	94.6 (9.5)	94.2 (4.2)	98.1 (7.1)	95.6 (2.2)	98.9 ± 6.9	108
	100	109 (1.7)	102 (2.5)	99.6 (3.2)	104 (4.7)	98.7 ± 6.1	103
Fluoranthene	20	92.0 (6.0)	89.4 (5.3)	95.7 (4.1)	92.4 (3.4)	102 ± 9.2	107
	100	103 (1.8)	108 (3.0)	98.1 (4.1)	103 (4.8)	96.0 ± 2.9	109
Pyrene	20	90.3 (5.6)	87.2 (7.4)	85.1 (4.5)	87.5 (3.0)	102 ± 4.8	110
	100	102 (1.8)	105 (2.5)	101 (2.9)	103 (2.0)	94.2 ± 9.2	106
Benzo(a)anthracene	20	89.3 (7.6)	93.2 (5.0)	94.5 (6.1)	92.3 (2.9)	80.6 ± 4.9	111
	100	98.5 (2.6)	100 (2.7)	99.5 (3.3)	99.3 (0.8)	106 ± 4.5	108
Benzo(b)fluoranthene	20	90.0 (7.5)	87.2 (4.3)	91.2 (5.2)	89.5 (2.3)	94.1 ± 2.6	103
	100	102 (1.4)	99.6 (3.3)	96.7 (4.1)	99.4 (2.7)	98.4 ± 3.6	104
Benzo(a)pyrene	20	92.6 (8.3)	102 (5.7)	95.1 (7.2)	96.6 (5.0)	75.1 ± 4.9	103
	100	101 (1.5)	99.8 (3.8)	97.5 (2.4)	99.4 (1.8)	103 ± 3.5	105
Indeno(1,2,3-cd)pyrene	20	88.1 (3.5)	84.1 (4.5)	91.1 (4.9)	87.8 (4.0)	79.8 ± 2.6	89.8
	100	101 (2.3)	103 (4.0)	105 (3.9)	103 (1.9)	92.2 ± 2.8	91.5
Dibenzo(ah)anthracene	20	108 (6.5)	110 (2.9)	101 (5.2)	109 (1.1)	98.9 ± 4.2	109
	100	107 (4.2)	109 (3.5)	110 (4.5)	109 (1.4)	99.4 ± 5.6	107
Benzo(ghi)perylene	20	102 (4.6)	108 (3.4)	106 (4.1)	105 (2.9)	97.5 ± 3.6	108
	100	111 (0.9)	106 (4.1)	110 (1.1)	109 (2.4)	99.0 ± 3.4	106

C - nominal concentration in ng/mg, n - number of measurements, ME - matrix effect

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645 **Table 4 Information on concentration levels for PAHs determined in real samples**

Analytes	Concentration [ng/mg], n=4											
	Sample ID											
	SU	5 cm/SU	SU	5 cm/SU	SU	5 cm/SU	SU	5 cm/SU	SU	5 cm/SU	SU	5 cm/SU
1	2	3	4	5	6	7	8	9	10	11	12	
Naphthalene	90.0±2.2	79.8±1.5	94.8±2.2	71.8±1.6	34.3±1.0	31.4±1.1	192±3.7	152±2.9	257±3.8	205±3.7	116±1.8	110±1.9
Acenaphthylene	100±2.3	89.5±1.6	105±2.3	79.8±1.3	37.6±1.3	33.1±1.0	214±3.9	169±2.8	283±4.2	225±3.6	129±2.6	122±2.0
2-Bromonaphthalene	97.6±2.4	86.9±1.4	106±1.9	77.7±1.4	35.9±1.0	32.4±1.4	232±4.1	174±2.1	332±4.3	238±3.8	128±2.9	123±2.1
Acenaphthene	91.6±2.0	82.2±1.5	97.8±2.2	74.2±1.6	35.5±1.2	32.2±1.2	203±3.9	159±2.2	280±4.0	215±3.9	119±2.2	112±2.0
Fluorene	70.6±1.6	62.4±1.3	76.1±1.5	57.5±1.2	25.7±1.1	23.6±1.1	154±2.6	123±1.7	212±4.1	163±3.6	91.2±1.6	86.3±1.3
Phenanthrene	105±2.4	91.9±2.4	108±1.8	81.6±1.5	35.4±1.0	33.6±1.0	228±4.1	183±3.7	307±4.3	242±4.2	133±2.3	129±2.9
Anthracene	101±2.3	88.9±2.2	107±2.0	81.4±1.3	35.1±1.4	31.5±1.4	215±3.6	177±2.6	287±3.8	231±3.7	129±2.5	124±2.5
Fluoranthene	103±1.9	90.1±1.4	107±1.9	82.3±1.4	35.8±1.1	33.7±1.2	229±4.1	179±2.2	312±4.2	241±4.3	131±2.2	127±2.2
Pyrene	98.4±2.0	85.7±1.3	103±1.7	78.3±1.3	34.5±1.0	33.0±1.1	216±3.7	170±2.8	297±4.3	229±4.2	125±2.1	120.7
Benzo(a)anthracene	108±2.3	93.8±1.6	114±1.8	86.9±1.5	35.4±1.2	23.90±0.93	247±3.8	192±3.9	341±4.5	260±3.8	138±2.9	135±2.5
Benzo(b)fluoranthene	99.2±2.4	86.6±1.5	105±2.3	80.8±1.6	33.4±1.1	30.9±1.1	229±3.9	178±2.8	317±4.2	241±4.1	127±2.6	125±2.1
Benzo(a)pyrene	106±1.9	93.3±2.4	113±2.0	84.8±1.9	33.7±1.0	31.0±1.2	248±4.1	192±3.6	342±4.5	260±3.8	138±2.9	135±2.2
Indeno(1,2,3-cd)pyrene	87.0±1.5	80.8±2.2	95.4±2.2	79.2±1.3	31.8±1.2	28.10±0.97	120±2.7	116±1.8	148±2.2	133±2.6	99.7±1.5	86.8±1.6
Dibenzo(ah)anthracene	143±2.9	134±2.9	128±2.9	133±2.9	59.2±1.2	54.2±1.2	209±3.9	199±3.7	260±4.2	236±3.9	170±2.8	146±2.9
Benzo(ghi)perylene	114±1.6	108±1.6	124±2.5	109±2.3	49.7±1.3	47.9±1.0	145±2.6	149±2.9	179±3.3	160±2.6	127±2.5	112±1.9
SU, surface of road; 5cm/SU, 5 cm under surface of road												

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