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

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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 ± 4.9 to 106.0 ± 4.5 %.

34 **Keywords**

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

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1. Introduction

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

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

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

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

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

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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. µ-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 µ-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 µg/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 µm, wall thickness: 100 µm) 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 glss/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 µg/cm3) 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**
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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 × 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 µL) was added into the vial to reconstitute the analytes.
155 The resulting extract was then transferred to 200 µL insert placed in autosampler vials and 2
156 µL 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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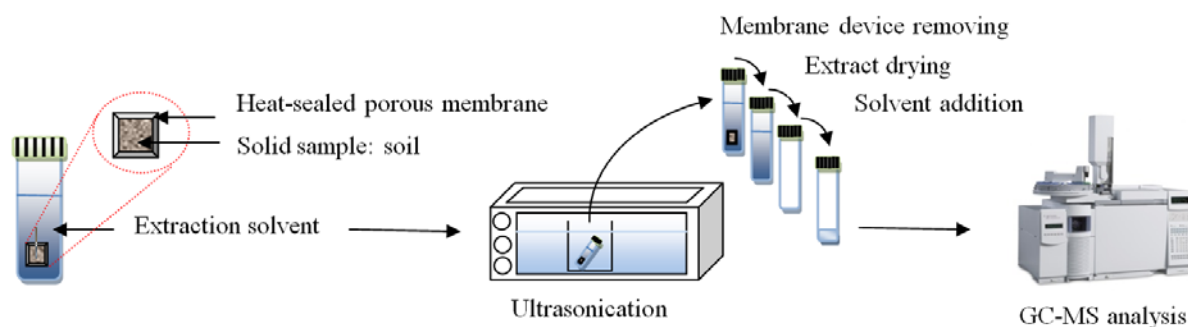
162
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166
167 Figure 1. The workflow of the developed analytical procedure for PAHs determination in soil
168 samples
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170 **2.4. Preparation of stock solutions, calibrators and quality control samples**

171 Stock solution of analytes was prepared in methanol by diluting the certified standard solution
172 to reach a concentration of 10 µg/mL. Stock solution of the IS was prepared also in methanol

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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.

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 µL 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

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

## 3. Results and discussion

3.1. Optimization of extraction procedure

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

3.1.1. Extraction solvent

The extraction solvent should be carefully selected as it has significant importance in extraction process. Affinity between extraction solvent and analytes in terms ofpolarity is an important parameter to consider. One mixture of organic solvents (acetone: n-hexane, 1:1 v/v) and three organic solvents and with varying polarity index (n-hexane, dichloromethane and toluene) were employed as extraction solvent. N-hexane was found the most effective compared to other examined solvents and it wasselected as an optimum extraction solvent (Fig. 2). PAHs were effectively extracted into n-hexane due to non-polar nature of both the PAHs and solvent.
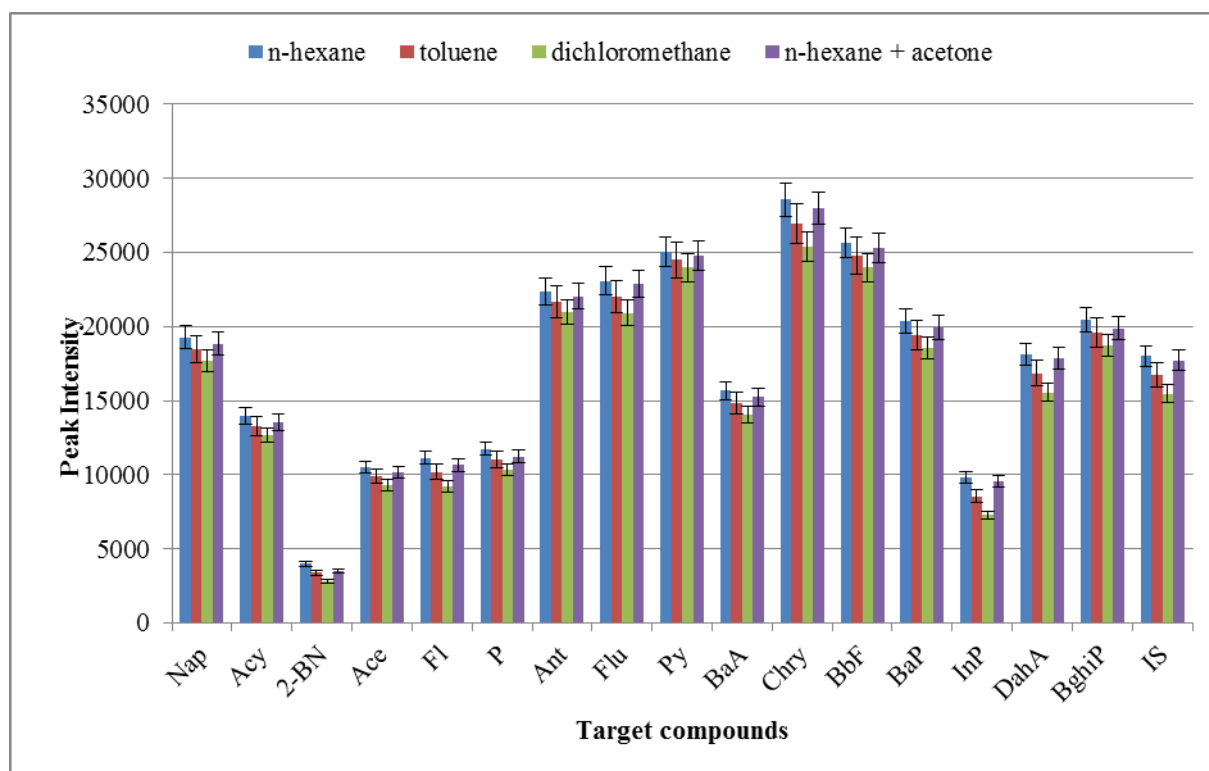
Figure 2. Selection of extraction solvent based on peak intensity for the determination of PAHs with ultrasound-assisted solvent extraction of porous membrane packed solid samples.

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

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

3.1.2. Time of extraction (ultra-sonication)

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

Hence, extraction time of 25 min was selected as optimum extraction time (Figure 3).
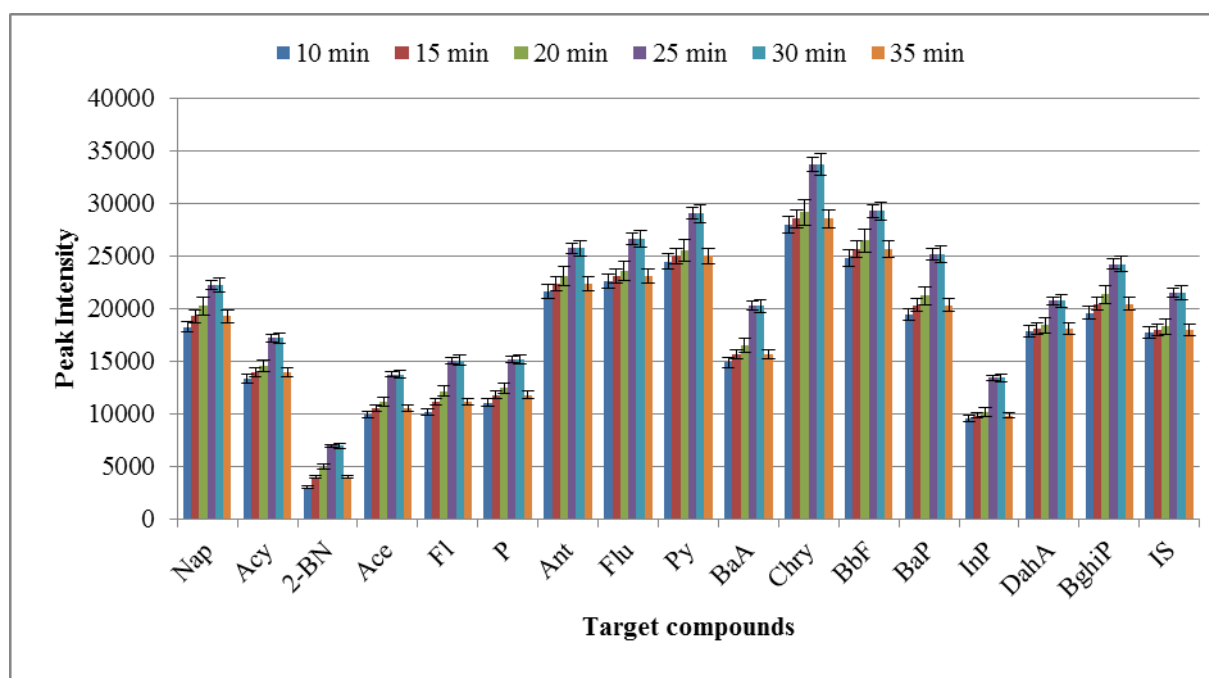
Figure 3. Selection of the extraction time based on peak intensity for the determination of PAHs with ultrasound-assisted solvent extraction of porous membrane packed solid samples.

3.1.3. Ultrasound power

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

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

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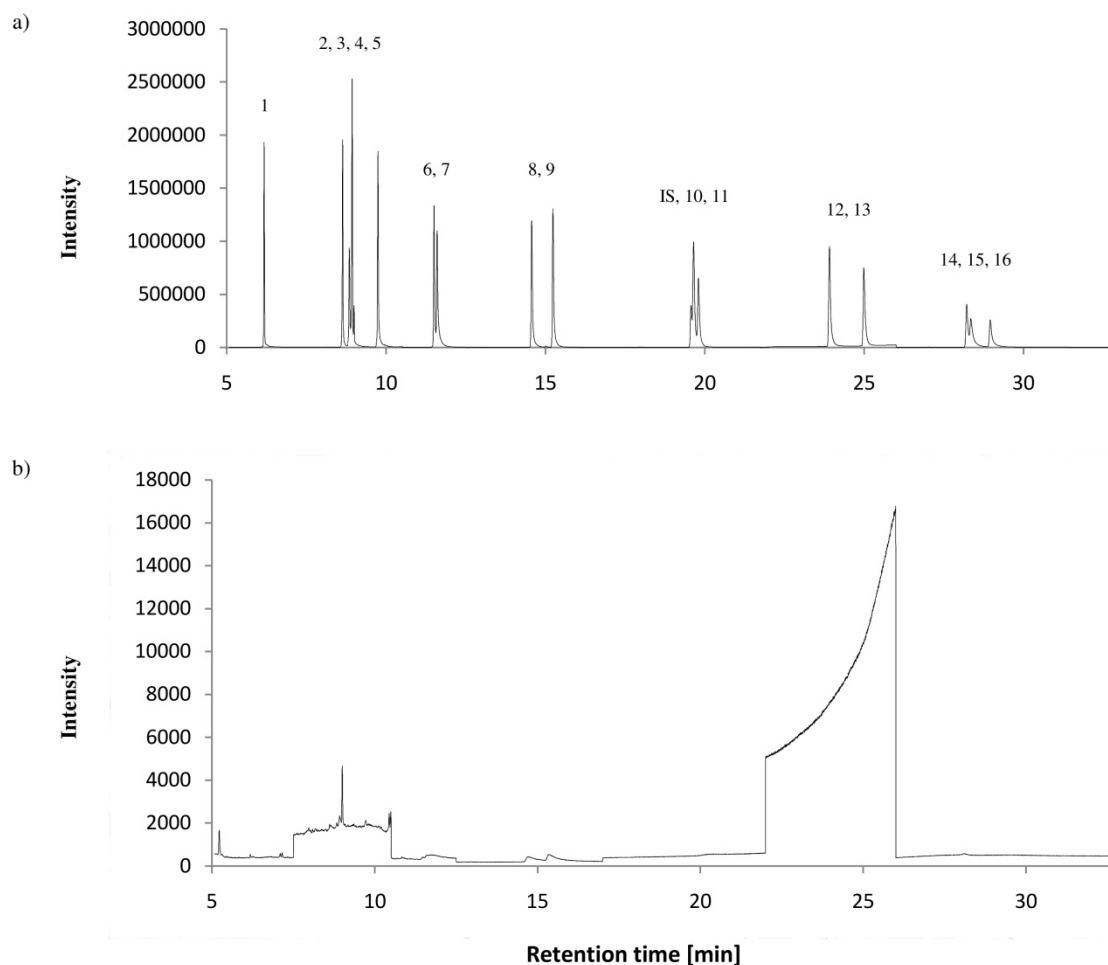
325 Based on the obtained validation parameters which fulfil the established international criteria
326 for analytical methods, it could be stated, that the presented method for the quantification of
327 PAH in soil samples is characterized by high accuracy and precision and can be used for the
328 analysis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

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a)

b)

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

3.3. Analysis of real samples

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

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

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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.

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-Wasylka 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 widndow (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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616 **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

617 *r* - Correlation coefficient, *LOD* - limit of detection, *LOQ* - limit of quantification
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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 ± 23	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

633 *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**

	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
Analytes	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	1202.7
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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