

This is the peer reviewed version of the following article:

Rattanakunsong N., Jullakan S., Plotka-Wasyłka J., Bunkoed O., A hierarchical porous composite magnetic sorbent of reduced graphene oxide embedded in polyvinyl alcohol cryogel for solvent-assisted-solid phase extraction of polycyclic aromatic hydrocarbons, JOURNAL OF SEPARATION SCIENCE (2022), pp.1-10, which has been published in final form at <https://dx.doi.org/10.1002/jssc.202200041>. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.

2 **A hierarchical porous composite magnetic sorbent of reduced graphene oxide**  
3 **embedded in polyvinyl alcohol cryogel for solvent assisted-solid phase extraction of**  
4 **polycyclic aromatic hydrocarbons**

5 Natnaree Rattanakunsong<sup>1</sup>, Sirintorn Jullakan<sup>1</sup>, Justyna Płotka-Wasyłka<sup>2</sup>, Opas Bunkoed<sup>1\*</sup>

6 <sup>1</sup>Center of Excellence for Innovation in Chemistry, Division of Physical Science, Faculty of  
7 Science, Prince of Songkla University, Hat Yai, Songkhla 90110, Thailand

8 <sup>2</sup>Department of Analytical Chemistry, Faculty of Chemistry and BioTechMed Center,  
9 Gdańsk University of Technology, 11/12 G. Narutowicza Street, 80-233 Gdańsk, Poland

10 **Running title: Porous composite sorbent for polycyclic aromatic hydrocarbons**

11  
12  
13 **Corresponding author:** Opas Bunkoed, Center of Excellence for Innovation in Chemistry,  
14 Division of Physical Science, Faculty of Science, Prince of Songkla University, Hat Yai,  
15 Songkhla 90110, Thailand, Email; Opas.b@psu.ac.th

16 Fax: +66 74558841

17  
18 **Abbreviations:** SPE, solid-phase extraction; PAHs, polycyclic aromatic hydrocarbons;  
19 rGOx, reduced graphene oxide; PVA, polyvinyl alcohol; CaCO<sub>3</sub>, calcium carbonate; Phe,  
20 Phenanthrene; Pyr, Pyrene; BaA, Benzo(a)anthracene; BbF, Benzo(b)fluoranthene; BaP,  
21 Benzo(a)pyrene

22 **Keywords:** Cryogel, polycyclic aromatic hydrocarbons, porous sorbent, reduced graphene  
23 oxide, solvent-assisted

## Abstract

24  
25 A hierarchical porous composite magnetic sorbent was fabricated and applied to the  
26 dispersive solvent assisted-solid phase extraction of five polycyclic aromatic hydrocarbons. A  
27 sorbent was first prepared by incorporating graphene oxide, calcium carbonate and magnetite  
28 nanoparticles into a polyvinyl alcohol cryogel. The graphene oxide was converted to reduced  
29 graphene oxide using ascorbic acid and a hierarchical porous structure was produced by  
30 reacting hydrochloric acid with incorporated calcium carbonate to generate carbon dioxide  
31 bubbles which created a second network. Before extracting the target analytes, extraction  
32 solvent was introduced into the hierarchical pore network of the sorbent. The extraction was  
33 based on the partition between the analytes and introduced extraction solvent and the  
34 adsorption of analytes on reduced graphene oxide. The extraction efficiency was enhanced  
35 through  $\pi$ - $\pi$  and hydrophobic interactions between polycyclic aromatic hydrocarbons and  
36 reduced graphene oxide and extraction solvent. The extracted polycyclic aromatic  
37 hydrocarbons were determined using HPLC coupled with fluorescence detector. The  
38 developed method was applied to extract polycyclic aromatic hydrocarbons in disposable  
39 diaper, coffee and tea samples and recoveries from 84.5 to 99.4% were achieved with relative  
40 standard deviations below 7%. The developed sorbent exhibited good reproducibility and can  
41 be reused for ten cycles.

42

43

44

45

46

47

48



49

## 50 1. Introduction

51 Polycyclic aromatic hydrocarbons (PAHs) are persistent organic environmental  
52 pollutants, generally produced by the incomplete combustion of organic matter or by high  
53 temperature pyrolysis during manufacturing processes [1]. PAHs are frequently found in  
54 industrial products and foods. Some PAHs have been classified as potential human  
55 carcinogens and the World Health Organization (WHO) has set the maximum permissible  
56 concentration of some PAHs in drinking water at  $0.2 \mu\text{g L}^{-1}$ . For this reason, the quantitative  
57 analysis of PAHs in certain matrices is of great importance. The determination of PAHs is  
58 normally performed with high performance liquid chromatography (HPLC) since the  
59 separation column used in this technique enables the simultaneous detection of several target  
60 PAHs with high sensitivity and good precision [2, 3]. However, target PAHs usually exist at  
61 trace concentrations in complex matrices and before chromatographic analysis can be  
62 performed, an appropriate extraction and enrichment process is normally required to reduce  
63 matrix interferences and increase the sensitivity of the response [4].

64 The extraction and enrichment of PAHs in various matrix samples can be  
65 accomplished with liquid-liquid extraction (LLE) [5], solid phase extraction (SPE) [4, 6],  
66 solid phase microextraction (SPME) [7], stir bar sorptive extraction (SBSE) [8] and magnetic  
67 solid phase extraction (MSPE) [9-11]. SPE is a widely used technique because it can be  
68 modified to improve extraction efficiency and the enrichment factor. Efficient analyte  
69 extraction with SPE requires a suitable adsorbent material and the choice of adsorbent  
70 material depends on the target molecule and the anticipated interactions between the target  
71 analyte and the adsorbent [12, 13]. Solid sorbents for the adsorption of PAHs have been  
72 fabricated using multiwalled carbon nanotubes [14], polyaniline [11], graphene [15],  
73 molecularly imprinted polymer [16] and covalent organic frameworks [17] but commercial



74 packed-particle SPE sorbents for the extraction of PAHs normally generate high back  
75 pressure, resulting in clogging of the cartridge. The use of a porous composite SPE sorbent is  
76 a more convenient approach that is able to overcome this drawback and improve extraction  
77 **performance** [18].

78 An alternative strategy that also improved the extraction efficiency of PAHs is a  
79 recently reported extraction technique that combined a liquid phase and a porous solid phase  
80 [19]. Using this technique, PAHs could be extracted from the sample solution based on the  
81 partition between the liquid phase, which is the extraction solvent, and the surface of the solid  
82 phase sorbent. Polyvinyl alcohol (PVA) cryogel is an interesting porous material since it can  
83 entrap other adsorption materials and also hold an extraction solvent [20, 21]. PVA cryogel  
84 can be easily prepared under cryogenic condition, and after thawing the ice crystals generated  
85 by freezing, the pores created can form the template for an interconnected hierarchical porous  
86 network [22]. A hierarchical porous PVA cryogel is a good choice for SPE and the extraction  
87 efficiency of PVA cryogel can be increased by incorporating hydrophobic material in a  
88 composite sorbent. A suitable hydrophobic material for this application is reduced graphene  
89 oxide (rGOx) which can adsorb PAHs via  $\pi$ - $\pi$  interaction [23].

90 In this work, an extraction solvent was introduced into a hierarchical porous  
91 composite monolith sorbent for the extraction and enrichment of PAHs. The sorbent was  
92 fabricated by incorporating rGOx, magnetite nanoparticles and  $\text{CaCO}_3$  into PVA cryogel  
93 (rGOx/ $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$ /PVA cryogel). The incorporation of  $\text{CaCO}_3$  enabled the creation of a  
94 porous network structure by reacting the  $\text{CaCO}_3$  embedded in the PVA cryogel with HCl to  
95 produce  $\text{CO}_2$  bubbles inside the sorbent. The porous composite sorbent was then soaked in  
96 extraction solvent. The developed solvent-assisted porous composite monolith sorbent was  
97 applied to extract and enrichment PAHs from samples of diaper material, tea and coffee. The  
98 extraction **performance** of the developed sorbent was compared with the **performance** of a



99 commercial sorbent. The developed method was successfully applied to extract PAHs in  
100 disposable diaper, coffee and tea samples.

## 101 **2. Materials and Methods**

### 102 **2.1 Chemicals and reagents**

103 Phenanthrene (Phe), Pyrene (Pyr), Benzo(a)anthracene (BaA), Benzo(b)fluoranthene  
104 (BbF) and Benzo(a)pyrene (BaP) were purchased from Restek (Bellefonte, USA). Acetic  
105 acid, ascorbic acid, hydrochloric acid, toluene and poly (vinyl alcohol) (PVA) ( $\geq 98\%$   
106 hydrolyzed) were from Merck (Darmstadt, Germany). Glutaraldehyde, iron (III) chloride  
107 hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), acetonitrile, methanol, and graphene oxide (15 - 20 sheets, 4 -10  
108 % edge-oxidized) were purchased from Sigma–Aldrich (Steinheim, Germany). Deionized  
109 water (DI) was produced from an ELGA Maxima ultrapure system (Buckinghamshire,  
110 England).

111 The individual stock standard solution of Phe, Pyr, BaA, BbF and BaP was prepared  
112 in acetonitrile at a concentration of  $1000 \text{ mg L}^{-1}$ . Working standard solutions of five PAHs  
113 were freshly prepared by serial dilution of the stock solutions with acetonitrile to the desired  
114 concentration.

### 115 **2.2. Samples**

116 Samples of disposable baby diapers ( 27), tea ( 5) and coffee ( 5) from many  
117 manufacturers typical for the specific type of sample were used for the analysis. The samples  
118 were stored in the original manufacturers' packaging at room temperature and protected from  
119 light.

### 120 **2.3 Instrumentation**

121 HPLC analysis of PAHs was performed on the Agilent 1100 series (Agilent  
122 Technologies Inc., Germany). PAHs were separated using a Fortis  $\text{C}_{18}$  column ( $5 \mu\text{m}$ ,  $150$   
123  $\text{mm} \times 4.6 \text{ mm i.d.}$ ). The mobile phase was water and acetonitrile (12:88 % v/v) passed at a



124 constant flow rate of 1.0 mL min<sup>-1</sup>. The injection volume was 20 μL and the column  
125 temperature was controlled at 30 °C. The responses of the target PAHs were measured by  
126 fluorescence detection. Excitation and emission wavelengths used are given in **Table S1**.

127 FTIR spectra were recorded by FTIR spectroscopy (PerkinElmer Waltham, MA,  
128 USA). Sorbent morphologies were determined by scanning electron microscopy (JSM-5200  
129 JEOL Tokyo, Japan). Nitrogen adsorption and desorption isotherms, and surface areas were  
130 measured using the Quantachrome Autosorb 1 system (Quantachome Instruments, USA).  
131 CHN elemental analysis was performed on a MACRO CHNS Analyzer (LECO, USA). TGA  
132 analysis was carried out using the TGA8000 apparatus (Perkin Elmer, USA).

#### 133 **2.4 Synthesis of magnetite nanoparticles**

134 Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> nanoparticles were synthesized following a reported procedure [14] with  
135 modification. The detail for the synthesis of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> is provided in the Supporting  
136 Information.

#### 137 **2.5 Fabrication of hierarchical porous composite monolith sorbent**

138 The fabrication procedure of the porous composite rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel  
139 sorbent is shown in **Fig. 1**. A homogenous PVA solution was obtained by stirring 2.0 g of  
140 PVA powder in 100 mL of DI water at 90°C for 20 min. The solution was allowed to cool  
141 down to room temperature and pH was adjusted to 1.0 with 0.5 M HCl. Subsequently, 0.2 g  
142 of the synthesized Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> nanoparticles, 5.0 mg of GOx, and 0.25 g of CaCO<sub>3</sub> were  
143 added to the PVA solution and stirred at 30 °C for 6 h. The composite cryogel sorbent was  
144 fabricated by dropping 0.20 mL of the mixture solution into the well of a 96-well plate,  
145 adding 5.0 μL of glutaraldehyde to the well, and freezing the solution at -20 °C for 12 h. The  
146 porous GOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/CaCO<sub>3</sub> PVA cryogel sorbent was obtained by thawing the frozen  
147 sorbent at room temperature (29 ± 2 °C). The thawed sorbent was removed from the plate and  
148 washed with DI water until pH was neutral (~5.5-7.0). The GOx incorporated in the obtained

149 cryogel sorbent was reduced to rGOx by heating the sorbent in 100 mL of 0.20% w/v  
150 ascorbic acid at 80 °C for 6 h. When the sorbent changed color from brown to black, a  
151 composite rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/CaCO<sub>3</sub> PVA cryogel sorbent was obtained. The sorbent was  
152 removed from the acid, washed with 50 mL of DI water and dried. The dried cryogel sorbent  
153 was then placed in 100 mL of HCl (20% w/v). The CaCO<sub>3</sub> in the composite sorbent reacted  
154 with the HCl to produce CO<sub>2</sub> bubbles which created a second pore system in the cryogel.  
155 Finally, the fabricated hierarchical porous composite cryogel sorbent was washed with DI  
156 water until pH was nearly neutral (~5.5-7).

## 157 **2.6 Solvent-assisted solid phase extraction**

158 The solvent assisted-SPE of PAHs using the porous rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel  
159 sorbent is illustrated in **Fig. 1A**. First, porous composite sorbents are placed in a glass bottle  
160 containing the extraction solvent and stirred for 30 min to allow the extraction solvent to  
161 diffuse and fill the pores of the sorbents. The pores of the sorbents retain the solvent through  
162 hydrophobic interaction with the rGOx. The composite sorbents, now charged with extraction  
163 solvent, are isolated using a magnet, transferred to 10.0 mL of sample solution in a vial and  
164 stirred for 15 min at 1000 rpm to extract the target analytes. The sorbents are isolated from  
165 the sample solution using a magnet, soaked in 2.0 mL of eluting solvent, sonicated for 5 min  
166 to elute PAHs and again isolated with a magnet. The eluting solvent is evaporated to dryness  
167 at 50 °C using a rotary evaporator. The residue is reconstituted in 0.5 mL of mobile phase  
168 and 20.0 µL are injected into the HPLC-FLD. The quality control of the developed method  
169 was considered from the blank extraction. To ensure that there is no contamination which  
170 may occur during the extraction, blank extraction was performed with deionized water and  
171 the whole procedure was conducted as described above.

172 To achieve the highest extraction efficiency, the following parameters were  
173 optimized: the amount of CaCO<sub>3</sub> and GOx incorporated in the PVA solution, the extraction

174 time, the stirring rate, the type of extraction solvent used, the volume of eluting solvent used,  
175 desorption time, sample volume and sample pH. Extraction **performance** was evaluated from  
176 extraction recovery (ER), which was determined according to the following equation:

$$177 \quad ER (\%) = (CV/C_X V_X) \times 100$$

178 where C and C<sub>x</sub> are the respective concentrations of PAHs in the reconstituted solvent ( $\mu\text{g L}^{-1}$ )  
179 and spiked sample, and V and V<sub>x</sub> are the volumes of the reconstituted solvent (0.50 mL)  
180 and the spiked sample, respectively.

## 181 **2.7 Preparation of diaper, coffee and tea samples**

182 Three parts of each diaper, the top sheet, inside, and back sheet, were cut into small  
183 pieces (0.5 cm x 0.5 cm) and mixed together at an average weight of approximately 0.40 g in  
184 a 50 mL centrifuge tube. Then, 8.0 mL of acetonitrile were added and the samples were  
185 extracted with ultrasonication for 30 min. This step was repeated two times and the collected  
186 supernatants were combined and evaporated to dryness at 60 °C using a rotary evaporator.  
187 The residue was dissolved in 0.50 mL of acetonitrile and diluted with 10 mL of DI water  
188 ready for solvent assisted-SPE. Tea and coffee samples were prepared using hot water. In 100  
189 mL of water at 95°C, 1.0 g of instant coffee was dissolved and stirred for 2 min. The solution  
190 was diluted 50 times before being extracted. Similarly, 1.0 g of dried tea leaves was soaked in  
191 100 mL of hot water at 95°C for 2 min. Tea leaves were removed by filtering the infusion  
192 through a 15  $\mu\text{m}$  filter paper. The liquid was allowed to cool to room temperature before  
193 being extracted by solvent assisted-SPE.

## 194 **3. Results and Discussion**

### 195 **3.1 Characterization of porous composite monolith sorbent**

196 The porous composite rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent was characterized  
197 using SEM, FTIR, TGA, CHN, BET and VSM techniques. SEM was used to investigate the  
198 surface morphology of the sorbent. SEM images (**Fig. 2A, B**) showed the high porosity of the



199 PVA cryogel which helps the sample solution pass through the sorbent easily. A photograph  
200 of the PVA cryogel is shown in **Fig. 2C**. The fabricated rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel  
201 sorbent exhibits a rough surface with a large surface area that aids analytes adsorption (**Fig.**  
202 **2D, E**). A photograph of the porous rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel adsorbent is shown in  
203 **Fig. 2F**.

204 The PVA cryogel, different elements of the fabricated sorbent, and the sorbent itself  
205 were characterized by FTIR spectroscopy. The FTIR spectrum of PVA cryogel (**Fig. S1A a**)  
206 shows adsorption bands at 3458 cm<sup>-1</sup> and 2948 cm<sup>-1</sup> related to -OH and -CH<sub>2</sub>- asymmetric  
207 stretching, respectively. The adsorption band at 1436 cm<sup>-1</sup> was assigned to C-H bending. The  
208 band at 1018 cm<sup>-1</sup> corresponds to the C-O group. The FTIR spectrum of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> (**Fig.**  
209 **S1A b**) shows bands at 3399 cm<sup>-1</sup> and 1626 cm<sup>-1</sup> that indicate the presence of -OH stretching  
210 vibrations due to the presence of hydroxyl. The adsorption bands at 592 cm<sup>-1</sup> and 1088 cm<sup>-1</sup>  
211 are due to the vibrations of Fe-O and Fe-O-Si stretching, respectively. In the spectrum of  
212 rGOx (**Fig. S1A c**), the bands at 1542 cm<sup>-1</sup> and 1192 cm<sup>-1</sup> correspond to C=C and C-OH,  
213 respectively. The FTIR spectrum of the porous composite rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel  
214 sorbent (**Fig. S1A d**) indicate that rGOx and Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> were successfully composited in the  
215 PVA cryogel.

216 CHN analysis was used to measure elemental carbon, nitrogen and hydrogen  
217 components of the porous composite sorbent. The results showed that the fabricated sorbent  
218 consisted of 58.87 % carbon, 0.02 % nitrogen and 7.76 % hydrogen.

219 The N<sub>2</sub> adsorption-desorption isotherm of the porous composite rGOx/Fe<sub>3</sub>O<sub>4</sub>-  
220 SiO<sub>2</sub>/PVA cryogel sorbent is shown in **Fig. S1B**. The results showed that the sorbent  
221 exhibited a type IV isotherm and a clear hysteresis loop was obtained, implying a  
222 mesoporous structure. The BET surface area of the sorbent was calculated as 6.7650 m<sup>2</sup> g<sup>-1</sup>.

223 To determine the thermal stability of the porous composite rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA  
224 cryogel sorbent, TGA analysis was performed from 25 to 900 °C. Since the TGA curve (**Fig.**  
225 **S1C**) indicated that no significant weight loss occurred up to 200 °C, the stability of the  
226 sorbent was considered sufficiently high for the intended extraction condition ( $27 \pm 2^\circ\text{C}$ ).

227 The saturation magnetization of the porous composite rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel  
228 sorbent was determined using a vibrating sample magnetometer (VSM). As shown in **Fig.**  
229 **S1D**, the saturation magnetization was about 2.290 emu g<sup>-1</sup> which is easily high enough for  
230 the sorbent to be separated from the solution with an applied magnet.

## 231 **3.2 Optimization of the sorbent synthesis and extraction conditions**

### 232 **3.2.1 Effect of amount of calcium carbonate**

233 Calcium carbonate (CaCO<sub>3</sub>) was incorporated into the composite sorbent to produce  
234 the hierarchical porous structure by reacting with HCl to produce CO<sub>2</sub> bubbles. The  
235 optimization of incorporated CaCO<sub>3</sub> was studied from 0.0 to 0.75% w/v (**Fig. 3A**). Extraction  
236 recovery was the determining parameter and this increased with increments of CaCO<sub>3</sub> up to  
237 0.25% w/v CaCO<sub>3</sub>. Recovery decreased at greater loadings of CaCO<sub>3</sub> because the sorbent  
238 became unstable and began to break up during stirring. Thus, 0.25% w/v of CaCO<sub>3</sub> was used  
239 for the fabrication of the porous rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent.

### 240 **3.2.2 Amount of graphene oxide**

241 The GO<sub>x</sub> incorporated in the composite sorbent was reduced to rGO<sub>x</sub>, which can  
242 interact with PAHs via  $\pi$ - $\pi$  interaction and can help to retain the extraction solvent in the  
243 pores of the sorbent through hydrophobic interaction. The optimization of the GO<sub>x</sub> loading  
244 was studied from 2 to 20 mg. The recoveries of PAHs increased with increments of GO<sub>x</sub> up  
245 to 5 mg and did not significantly change at larger loadings (**Fig. 3B**). Therefore, 5 mg of GO<sub>x</sub>  
246 was the optimal loading.

### 247 **3.2.3 Extraction time**

248 The duration of the solvent assisted-SPE of PAHs using the porous composite  
249 rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent was varied from 10 to 30 min to obtain the highest  
250 recovery of PAHs. At 15 min, recoveries of all PAHs were higher than they were at 10 min,  
251 but remained constant after 15 min (**Fig. 3C**). Consequently, 15 min was selected as the  
252 optimal extraction time.

### 253 3.2.4 Effect of stirring rate

254 The stirring rate of the sample solution can affect the contact rate between the  
255 analytes and the sorbent, or the acceptor phase. In this work, the stirring rate of the sample  
256 solution was optimized between 500 and 1500 rpm. The highest extraction recoveries for all  
257 target PAHs was obtained at 1000 rpm (**Fig. 3D**). Lower recoveries were obtained at slower  
258 and faster stirring rates. At slower rates the low recoveries were perhaps due to insufficient  
259 contact rates between the analytes and liquid and solid acceptor phases. The lower recoveries  
260 at stirring rates above 1000 rpm may have been due to the reduced contact between the  
261 analytes and extraction phases. Also, too fast a stirring rate can cause extraction solvent to be  
262 discharged from the pores of the sorbent. Therefore, the optimal stirring rate of the sample  
263 solution was 1000 rpm.

### 264 3.2.5 Effect of type of extraction solvent

265 PAHs are non-polar compounds. The extraction solvent used to assist the extraction  
266 of PAHs from the sample solution, was selected after investigating the extraction  
267 **performance** achieved using acetonitrile, methanol, toluene, acetonitrile+toluene (1:1, v/v)  
268 and methanol+toluene (1:1, v/v) (**Fig. S2A**). The mixture of acetonitrile and toluene (1:1, v/v)  
269 provided the highest extraction recovery for all target PAHs, and therefore this was the  
270 solvent introduced into the pores of the porous composite rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel  
271 sorbent to assist extraction.

### 272 3.2.6 Volume of eluting solvent

273 At the end of the extraction cycle, the adsorbed PAHs were eluted from the pores of  
274 the sorbent using a mixture of acetonitrile and toluene (1:1, v/v). The volume of solvent used  
275 to elute the adsorbed PAHs was optimized from 1.0 to 4.0 mL (**Fig. S2B**) to obtain the lowest  
276 solvent consumption that could achieve a good extraction recovery. Recoveries of the five  
277 target PAHs increased with the increment of eluent volume from 1.0 to 2.0 mL and was  
278 unchanged above 2.0 mL. Thus, 2.0 mL of the mixture of acetonitrile and toluene (1:1, v/v)  
279 was selected to elute target PAHs from the fabricated sorbent.

### 280 **3.2.7 Effect of desorption time**

281 The optimization of the time required to desorb PAHs from the porous composite  
282 rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent was studied under sonication from 1 to 20 min and  
283 the results are shown in **Fig. S2C**. The desorption of all target PAHs was completed after 5  
284 min. The highest recoveries could therefore be obtained with a desorption time of 5 min.

### 285 **3.2.8 Effect of sample volume**

286 Sample volume normally affects the enrichment and extraction of analytes. Larger  
287 sample volumes provide higher enrichment factors which can help detect analytes at low  
288 concentrations. However, if the sample volume is too large, extraction recoveries can be low.  
289 Therefore, to achieve a high enrichment factor with satisfactory recoveries, the sample  
290 volume must be accurately optimized. In this work, sample volume was investigated from 5  
291 to 20 mL. The optimal sample volume was 10 mL, which provided acceptable recoveries  
292 with a high enrichment factor (**Fig. S2D**).

### 293 **3.2.9 Effect of sample pH**

294 Sample pH can affect the extraction of analytes and the stability of the sorbent. Since  
295 PAHs are aromatic compounds, sample pH does not affect their structure but the stability and  
296 other properties of the sorbent may be affected. Therefore, the effect of sample solution pH  
297 was investigated between pH 3 and 11 and the results demonstrated that recoveries were not



298 significantly changed within the studied range (**Fig. S3**). This finding confirmed that the  
299 fabricated composite sorbent can be used to extract PAHs in sample solutions within a wide  
300 pH range without the need to adjust the sample solution pH.

### 301 **3. 3 Comparison of various polyvinyl alcohol cryogel sorbents**

302 The PVA cryogel sorbent was evaluated at different stages of fabrication. The five  
303 target PAHs were extracted with hierarchically porous sorbents of Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA,  
304 GOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA and rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA. The rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA sorbent  
305 exhibited the best extraction efficiency for all target PAHs (**Fig. S4**) due to the greater  
306 hydrophobicity of reduced graphene oxide compared to graphene oxide. The extraction  
307 efficiency of the Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA sorbent was low due to its greater polarity, which inhibits  
308 interactions with less polar compounds.

### 309 **3.4 Analytical performance**

310 The developed porous composite rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent was coupled  
311 with HPLC analysis to determine the analytical performance of the system. The developed  
312 method demonstrated good linearity of BaA from 0.34-500.0 µg kg<sup>-1</sup> of diaper material and  
313 from 1.7 -500.0 µg L<sup>-1</sup> of coffee and tea. For the determination of Phe, BbF and BaP, the  
314 method showed linearity from 0.50-500.0 µg kg<sup>-1</sup> of diaper material and from 3.4-500.0 µg L<sup>-1</sup>  
315 of coffee and tea. For the determination of Pyr, the response was linear from 1.67-500.0 µg  
316 kg<sup>-1</sup> of diaper material and from 5.0-500.0 µg L<sup>-1</sup> of coffee and tea. The calculation of LODs  
317 was based on a signal-to-noise (S/N) ratio of 3. The LODs were 0.10-0.50 µg kg<sup>-1</sup> for diaper  
318 material and 0.5-1.5 µg L<sup>-1</sup> for both coffee and tea. The calculation of LOQs was based on an  
319 S/N of 10. The LOQs were 0.34-1.67 µg kg<sup>-1</sup> for diaper and 1.7-5.0 µg L<sup>-1</sup> for coffee and tea  
320 (**Table 1**).

### 321 **3.5 Analysis of polycyclic aromatic hydrocarbons in disposable baby diapers, coffee and** 322 **tea**



323 The developed method was applied to extract and determine PAHs in samples of  
324 single-use diaper material (27 samples), coffee (5 samples) and tea (5 samples). The  
325 preparation of all samples was described in **Section 2.7**. The HPLC chromatograms of diaper  
326 material, coffee and tea are shown in **Fig. S5**. Five PAHs were found in baby diaper between  
327 8.1 and 177.9  $\mu\text{g kg}^{-1}$ , BaA, BbF and BaP were found in coffee and tea samples between 4.2  
328 and 22.0  $\mu\text{g L}^{-1}$ . The accuracy of the developed method was evaluated by determining the  
329 relative recoveries of PAHs from spiked samples at different concentrations and relative  
330 recoveries are summarized in **Table S2**. The relative recoveries of all target PAHs were in the  
331 range of 84.5 to 99.4% with RSDs of 0.9-6.5%. These results confirmed that the developed  
332 method has a good accuracy and can be applied to extract and determine PAHs in various  
333 sample matrices.

### 334 **3.6 Reproducibility and Reusability**

335 The fabrication reproducibility of the porous composite  $\text{rGO}_x/\text{Fe}_3\text{O}_4\text{-SiO}_2/\text{PVA}$   
336 sorbent was evaluated by preparing six different lots of sorbent using the same procedure.  
337 The fabricated sorbents were used to extract the target PAHs and the results are presented in  
338 **Fig. S6**. The RSDs of all target PAHs were between 0.75 and 2.70 % which confirmed the  
339 good reproducibility of the fabrication process, which contributes to the good precision of the  
340 method.

341 The reusability of the fabricated sorbent was also evaluated to reduce fabrication time,  
342 material costs and chemicals used. After being applied to extract PAHs, the used sorbent was  
343 cleaned with 1.0 mL of the extraction solvent, rinsed with 5.0 mL of DI water and then used  
344 to extract PAHs for another extraction/desorption cycle. The extraction recovery of PAHs  
345 was better than 80% up to the tenth extraction cycle (**Fig. S7**). The reduction in recovery after  
346 10 extraction cycles may have been due to the loss of  $\text{rGO}_x$  from the composite sorbent  
347 during desorption and washing. Perhaps some interfering species in the samples were



348 adsorbed on the surfaces of the sorbent and reduced the number of active adsorption sites for  
349 target PAHs. We concluded that the developed porous composite rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA  
350 cryogel sorbent can be reused for 10 cycles of extraction and desorption.

### 351 **3.7 Comparison with commercial sorbent and other works**

352 The analytical **performance** and accuracy of the developed method were compared  
353 with the **performance** and accuracy of an octadecyl (C<sub>18</sub>) modified silica sorbent and the  
354 results are presented in **Fig. S8**. Both the developed sorbent and the C<sub>18</sub> modified silica  
355 sorbent achieved recoveries better than 80% for all target PAHs. These results confirm that  
356 the developed method is accurate and can be applied to extract PAHs in real samples. The  
357 advantages of the present method include simple preparation, convenience of use, reusability  
358 and high efficiency. The **performance** of the developed method was compared with the  
359 **performance** of other reported methods and the comparative study is summarized in **Table**  
360 **S3**. The LOD and extraction recovery of the developed method are better than or comparable  
361 with other methods. Therefore, the hierarchically porous composite rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA  
362 cryogel sorbent can be used to extract PAHs from complex samples for subsequent analysis.

### 363 **4. Concluding remarks**

364 A solvent assisted-solid phase extraction method was successfully developed and  
365 applied to extract, preconcentrate and determine polycyclic aromatic hydrocarbons. The  
366 developed method integrated solvent assisted and solid phase extraction strategies. A porous  
367 composite sorbent was prepared by incorporating graphene oxide into a PVA solution that  
368 was then subjected to cryogelization and thawing. The graphene oxide was converted to  
369 reduced graphene oxide with ascorbic acid. A hierarchical porous network was generated by  
370 incorporating CaCO<sub>3</sub> into the cryogel and then reacting it with HCl to create CO<sub>2</sub> bubbles  
371 that generated a second network of smaller pores. Magnetite nanoparticles were also caged  
372 into the PVA cryogel to produce a magnetic sorbent for simple and rapid isolation from



373 sample solutions. The SPE was assisted by introducing an extraction solvent into the  
374 hierarchical porous network of the composite sorbent. The developed extraction method  
375 achieved recoveries of polycyclic aromatic hydrocarbons from 84.5 to 99.4%. This developed  
376 porous composite sorbent can be used to extract trace polycyclic aromatic hydrocarbons and  
377 can also be modified to extract less polar compounds.

### 378 **Acknowledgements**

379 This research was supported by the Research Fellowship, Faculty of Science, Prince  
380 of Songkla University (contract no. SCI64002) and The Center of Excellence for Innovation  
381 in Chemistry (PERCH-CIC). This work was also supported by the National Science Center in  
382 Poland granted on the basis of the decision number DEC-2020/37/B/ST4/02886 project  
383 number UMO-2020/37/B/ST4/02886. Mr. Thomas Duncan Coyne is also acknowledged for  
384 assistance with the English text of this manuscript.

### 385 **Conflict of interest**

386 The authors declare that they have no competing interests.

### 387 **References**

- 388 1. Shi Z., Jiang J., Pang W., Ma H., Chu X., Zhou C., Zhang H., Dispersive micro-solid phase  
389 extraction using cotton based carbon fiber sorbent for the determination of three polycyclic  
390 aromatic hydrocarbons in tea infusion by gas chromatography-quadrupole mass spectrometry.  
391 *Microchem. J.* 2019, *151*, 104209.
- 392 2. Li L., Han D., Wang M., Han Y., Yan H., Molybdenum disulfide-hypercrosslinked  
393 polymer composite as an adsorbent for determination of polycyclic aromatic hydrocarbons in  
394 environmental water coupled with HPLC-FLD. *Microchim. Acta* 2020, *187*, 242.
- 395 3. Fan C., Cao X., Han T., Pei H., Hu G., Wang W., Qian C., Selective microextraction of  
396 polycyclic aromatic hydrocarbons using a hydrophobic deep eutectic solvent composed with  
397 an iron oxide-based nanoferrofluid. *Microchim. Acta* 2019, *18*, 560.



- 398 4. Zhang X., Shen Y.F., Li X.X., Yang J.R., Liu Z.S., Huang Y.P., Preparation of gold  
399 nanorod-incorporated monolith for solid phase extraction of polycyclic aromatic  
400 hydrocarbons. *Microchim. Acta* 2020, 187, 418.
- 401 5. Wu S., Yu W., Liquid–liquid extraction of polycyclic aromatic hydrocarbons in four  
402 different edible oils from China. *Food Chem.* 2012, 134, 597-601.
- 403 6. Shen Y.F., Zhang X., Mo C.E., Huang Y.P., Liu Z.S., Preparation of graphene oxide  
404 incorporated monolithic chip based on deep eutectic solvents for solid phase extraction. *Anal.*  
405 *Chim. Acta* 2020, 1096, 184-192.
- 406 7. Chen J., Zhang B., Dang X., Zheng D., Ai Y., Chen H., A nanocomposite consisting of  
407 etched multiwalled carbon nanotubes, amino-modified metal-organic framework UiO-66 and  
408 polyaniline for preconcentration of polycyclic aromatic hydrocarbons prior to their  
409 determination by HPLC. *Microchim. Acta* 2020, 18, 78.
- 410 8. Vallez-Gomis V., Grau J., Benede J.L., Chisvert A., Salvador A., Reduced graphene oxide-  
411 based magnetic composite for trace determination of polycyclic aromatic hydrocarbons in  
412 cosmetics by stir bar sorptive dispersive microextraction. *J. Chromatogr. A* 2020, 1624,  
413 461229.
- 414 9. Nian Q., Wang X., Wang M., Zuo G., A hybrid material composed of graphitic carbon  
415 nitride and magnetite ( $\text{Fe}_3\text{O}_4$ ) for magnetic solid-phase extraction of trace levels of  
416 hydroxylated polycyclic aromatic hydrocarbons. *Microchim. Acta* 2019, 186, 497.
- 417 10. Nascimento M.M., Olimpio da Rocha G., Bittencourt de Andrade J., Simple and effective  
418 dispersive micro-solid phase extraction procedure for simultaneous determination of  
419 polycyclic aromatic compounds in fresh and marine waters. *Talanta* 2019, 204, 776-791.
- 420 11. Nurerk P., Kanatharana P., Bunkoed O., Polyaniline-coated magnetite nanoparticles  
421 incorporated in alginate beads for the extraction and enrichment of polycyclic aromatic  
422 hydrocarbons in water samples. *Int. J. Environ. Anal. Chem* 2017, 97, 145-158.



- 423 12. Bunkoed O., Rueankaew T., Nurerk P., Kanatharana P., Polyaniline-coated cigarette  
424 filters as a solid-phase extraction sorbent for the extraction and enrichment of polycyclic  
425 aromatic hydrocarbon in water samples. *J. Sep. Sci.* 2016, 39, 2332-2339.
- 426 13. Kamran M., Dauda M., Basheer C., Siddiqui M.N., Lee H.K., Highly efficient porous  
427 sorbent derived from asphalt for the solid-phase extraction of polycyclic aromatic  
428 hydrocarbons. *J. Chromatogr. A* 2020, 1631, 461559.
- 429 14. Bunkoed O., Kanatharana P., Extraction of polycyclic aromatic hydrocarbons with a  
430 magnetic sorbent composed of alginate, magnetite nanoparticles and multiwalled carbon  
431 nanotubes. *Microchim. Acta* 2015, 182, 1519-1526.
- 432 15. Gao Y., Qin Y., Xiong F., Zhao L., Determination of trace polycyclic aromatic  
433 hydrocarbons in water and milk using solid-phase extraction packed with graphene/chitosan  
434 composite aerogel prior to gas chromatography–mass spectrometry. *J. Sep. Sci.* 2020, 43,  
435 3940-3948.
- 436 16. Saad N., Chaaban M., Patra D., Ghanem A., El-Rassy H., Molecularly imprinted phenyl-  
437 functionalized silica aerogels: Selective adsorbents for methylxanthines and PAHs.  
438 *Microporous Mesoporous Mater.* 2020, 292, 109759.
- 439 17. Yu J., Di S., Ning T., Yang H., Zhu G.T., Chen P., Yu H., Wang J., Zhu S., Rational  
440 design and synthesis of magnetic covalent organic frameworks for controlling the selectivity  
441 and enhancing the extraction efficiency of polycyclic aromatic hydrocarbons. *Microchim.*  
442 *Acta* 2020, 187, 531.
- 443 18. Noosang S., Bunkoed O., Thavarungkul P., Kanatharana P., New sulfonate composite  
444 functionalized with multiwalled carbon nanotubes with cryogel solid-phase extraction sorbent  
445 for the determination of  $\beta$ -agonists in animal feeds. *J. Sep. Sci.* 2015, 38, 1951-1958.
- 446 19. Jullakan S., Bunkoed O., Pinsrithong S., Solvent-assisted dispersive liquid-solid phase  
447 extraction of organophosphorus pesticides using a polypyrrole thin film–coated porous



- 448 composite magnetic sorbent prior to their determination with GC-MS/MS. *Microchim. Acta*  
449 2020, 187, 677.
- 450 20. Wang Y., Jia M., Wu X., Wang T., Wang J., Hou X., PEG modified column MIL-  
451 101(Cr)/PVA cryogel as a sorbent in stir bar solid phase extraction for determination of non-  
452 steroidal anti-inflammatory drugs in water samples. *Microchem. J.* 2019, 146, 214-219.
- 453 21. Wang Y., Zhang Y., Cui J., Li S., Yuan M., Wang T., Hu Q., Hou X., Fabrication and  
454 characterization of metal organic frameworks/ polyvinyl alcohol cryogel and their application  
455 in extraction of non-steroidal anti-inflammatory drugs in water samples. *Anal. Chim. Acta*  
456 2018, 1022, 45-52.
- 457 22. Chullasat K., Nurerk P., Kanatharana P., Kueseng P., Sukchuay T., Bunkoed O., Hybrid  
458 monolith sorbent of polypyrrole-coated graphene oxide incorporated into a polyvinyl alcohol  
459 cryogel for extraction and enrichment of sulfonamides from water samples. *Anal. Chim. Acta*  
460 2017, 961, 59-66.
- 461 23. Fumes B.H., Lanças F.M., Use of graphene supported on aminopropyl silica for  
462 microextraction of parabens from water samples. *J. Chromatogr. A* 2017, 1487, 64-71.

463

#### 464 **Figure captions**

465 **Fig. 1** Diagram (A) shows the procedures for the fabrication of the porous composite  
466 rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent and the dispersive solvent assisted-solid phase  
467 extraction of PAHs. Diagram (B) shows the formation of the hierarchically porous  
468 rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent.

469 **Fig. 2** SEM images (A) and (B) are of PVA cryogel at magnifications of 100X and 10,000X  
470 and the photograph (C) is of the PVA cryogel monolith. SEM images (D) and (E) are of the  
471 porous composite rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent at magnifications of 100X and  
472 10,000X, and the photograph (F) is of the porous rGO<sub>x</sub>/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA sorbent.



473 **Fig. 3** Five polycyclic aromatic hydrocarbons in solution were extracted by solvent assisted-  
474 solid phase extraction using a porous composite rGOx/Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub>/PVA cryogel sorbent.  
475 Charts (A) and (B) show the effect on extraction recovery of the CaCO<sub>3</sub> and GOx loadings  
476 used in the sorbent fabrication. Charts (C) and (D) show the effect on recovery of extraction  
477 time and stirring rate used during the extraction procedure.

478

479

480

481

482

483

484

485

486