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A sensitive microextraction by packed sorbent-gas chromatography-mass spectrometry method for the assessment of polycyclic aromatic hydrocarbons contamination in Antarctic surface snow

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1	A sensitive microextraction by packed sorbent-gas chromatography-mass
2	spectrometry method for the assessment of polycyclic aromatic hydrocarbons
3	contamination in Antarctic surface snow
4	
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27 ABSTRACT

For the first time an eco-friendly method involving microextraction by packed sorbent (MEPS) 28 coupled to gas chromatography-mass spectrometry (GC-MS) was developed for the determination of 29 30 the 16 US-EPA priority pollutant polycyclic aromatic hydrocarbons (PAHs) as indicators of anthropogenic contamination in snow samples collected in polar regions. MEPS was carried out by 31 32 using C8 sorbent material packed in a barrel insert and needle (BIN) and integrated in the eVol® semi-33 automatic device. For optimization purposes a Face Centred Design and the multicriteria method of the desirability functions were performed to investigate the effect of some parameters affecting the 34 35 MEPS extraction efficiency, i.e. the number of loading cycles and the number of elution cycles. The 36 developed MEPS-GC-MS method proved to be suitable for PAHs analysis at ultra-trace level by extracting small sample volumes achieving detection limits for 16 PAHs in the 0.3 - 5 ng L⁻¹ range, 37 repeatability and intermediate precision below 11% and 15%, respectively, and good recovery rates 38 in the 77.6 (\pm 0.1)–120. 8 (\pm 0.1)% range for spiked blank snow samples. Enrichment factors in the 39 64 (\pm 7)–129 (\pm 18) range were calculated. Finally, the proposed method was successfully applied to 40 41 the determination of PAHs in surface snow samples collected in 2020 – 2021 from four locations of Northern Victoria Land, Antarctica. Local emission sources such as ships and research stations were 42 found to influence PAHs concentrations in the surface snow. 43

44 Keywords:

- 45 Microextraction by packed sorbents
- 46 Gas chromatography–mass spectrometry
- 47 Polycyclic aromatic hydrocarbons
- 48 Antarctica
- 49 Snow

50 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds that consist of two or 51 more aromatic rings and have both natural and anthropogenic sources (Srogi, 2007). PAHs include 52 16 priority pollutants regulated by the U.S. Environmental Protection Agency (US-EPA) due to their 53 potential toxicity in humans and other organisms as well as their occurrence and ubiquity in the 54 55 environment (Hussar et al., 2012; U.S. Environmental Protection Agency, 2014). As PAHs are semivolatile compounds, they are subject to long-range transport from emission sources to remote areas 56 (Wang et al., 2009; Korosi et al., 2015), i.e. places with a minimum contribution of anthropogenic 57 emissions such as Arctic and Antarctica (Baltensperger and Furger, 2008) or high altitude 58 environments like Alps and Caucasus (Gabrieli et al. 2010a; Vecchiato et al., 2020). In these regions, 59 60 low temperatures cause the deposition of organic compounds and their accumulation in the polar environment (Cao et al., 2018), producing a snow stratification which reveals the chemical 61 composition of the atmosphere at the time of the deposition (Legrand and Mayewski, 1997). 62 63 Therefore, PAHs play an important role in paleoenvironmental studies being considered tracers of 64 both anthropogenic fossil fuel combustion and global natural events (Giannarelli et al., 2017; Giorio et al., 2018). Several investigations have been focused on their distribution patterns, seasonal 65 depositions and accumulation trends in order to obtain chemical records and the assessment of 66 67 contamination sources (Jaffrezo et al., 1994; Wang et al., 2009; Kukučka et al., 2010; Giannarelli et al., 2017; Cao et al., 2018; Vecchiato et al., 2018). However, it should be noted that the analysis of 68 PAHs in ice and snow samples requires high sensitivity and selectivity due to the presence of these 69 70 compounds at ultra-trace levels. In addition, sample volume is a critical issue because low sample 71 volume is fundamental to obtain an adequate temporal resolution of the glacial stratification (Barbante 72 et al., 2017), thus challenging the applicability of sample preparation methods to paleoclimatic 73 investigation of organic compounds (Gabrielli and Vallelonga, 2015).

74 Liquid-liquid extraction (LLE) (Brum et al., 2008; Dasgupta et al., 2011) and solid-phase extraction 75 (SPE) (Ma et al., 2010; Okoli et al., 2016) are the most commonly used to extract and preconcentrate PAHs from water samples. Nevertheless, these methods are time-consuming and require large sample 76 77 volumes, so they are difficult to apply to obtain a proper temporal resolution in the analysis of snow samples. These drawbacks are overcome by the development of cost-effective and environmental 78 79 friendly analytical methods based on miniaturized techniques to improve the classical procedures 80 used for sample treatment in environmental analysis. Miniaturization of the sample treatment technique allows the use of small sample volumes and its feasible manipulation in a miniaturized 81 environment, the reduction of the number of steps required for sample preparation and the 82 consumption of a low amount of organic solvents, providing a greener approach for analytical 83 procedures (Ramos et al., 2005; Płotka-Wasylka et al., 2015). 84

Microextraction by packed sorbent (MEPS) was first developed by Abdel-Rehim as a miniaturization 85 86 of conventional SPE technique (Abdel-Rehim, 2004), allowing the integration of sampling, clean-up and pre-concentration of the analytes into a single device (Moein et al., 2015). In MEPS, 1 - 4 mg of87 88 the sorbent material is packed inside a syringe as a plug or in the barrel insert and needle called BIN, enabling for a semi or fully automated system (Abdel-Rehim, 2011; Moein et al., 2015). The small 89 amount of sorbent used in MEPS can easily be washed and reused more than 300 times for water 90 sample analysis (Moein et al., 2015). A key-point of this miniaturized technique is the possibility to 91 92 handle very low sample volume, i.e., a few microliters. Thus, at first MEPS was attractive for bioanalysis application, since the sample volume available for testing body fluids is limited (Pereira 93 et al., 2014; Woźniakiewicz et al., 2014; Saracino et al., 2015; Fernández et al., 2017; Bianchi et al., 94 95 2019). Nevertheless, MEPS has also been applied to environmental analysis in order to reduce the extraction time and to enhance the degree of automation and sensitivity (Moeder et al., 2010; Prieto 96 97 et al., 2011). Although different studies described MEPS procedures for the determination of PAHs in water samples (El-Beggali et al., 2006; Prieto et al., 2010; Fu et al., 2012; Quinto et al., 2012, 2014; 98

99 Yang et al., 2017), up to date, the application of this technique has not been reported for paleoclimatic100 purposes, despite the acknowledged advantages.

The present study is part of a research project that aimed to develop innovative analytical methods 101 102 and miniaturized procedures for sample preparation, investigate new chemical proxies and, lastly, characterize the chemical load present in ice cores (Arcoleo et al., 2020). Thereby, the aim of the 103 herein described work was the development and optimization of a semi-automatic MEPS-GC-MS 104 105 method to determine the 16 priority PAHs in Antarctic water samples as paleoenvironmental proxies. To best of our knowledge, the use of miniaturized techniques for pre-treatment of polar water samples 106 is scarce, particularly for the determination of PAHs present in ice cores and snow samples. In this 107 108 study, a fast and ultra-sensitive MEPS-GC-MS analytical method was established and successfully applied to the analysis of five surface snow samples from Antarctica. 109

110 2. Material and methods

111 2.1. Chemicals and reagents

The standard mixture of 16 PAHs including naphthalene (Nap), acenaphthene (Ace), fluoranthene 112 (Flt), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), pyrene (Py), 113 benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene 114 (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InPy), dibenzo[a,h]anthracene (DiahA) and 115 benzo[g,h,i]perylene (BghiP) (each component at a concentration of 100 µg mL⁻¹ in acetonitrile), and 116 deuterated PAHs internal standard (IS) containing naphthalene-d8 (Nap-d8), acenaphthene-d10 (Ace-117 d10), phenanthrene-d10 (Phe-d10), anthracene-d10 (Ant-d10), benzo[a]anthracene-d12 (BaA-d12), 118 119 chrysene-d12 (Chr-d12) benzo[g,h,i]perylene-d12 (BghiP-d12), dibenzo[a,h]anthracene-d14 (DiahA-d14), acenaphthylene-d8 (Acy-d8), fluorene-d10 (Flu-d10), fluoranthene-d10 (Flt-d10), 120 pyrene-d10 (Py-d10), benzo[a]pyrene-d12 (BaP-d12), benzo[b]fluoranthene-d12 (BbF-d12), 121 benzo[k]fluoranthene-d12 (BkF-d12) and indeno[1,2,3-c,d]pyrene-d12 (InPy-12) (each component at 122

a concentration of 10 μ g mL⁻¹ in acetonitrile) were purchased from Neochema (Bodenheim, Germany) and were stored in the absence of light at 4 °C.

Hexane (puriss. p.a., ACS reagent, ≥99.0% GC), ethyl acetate (EtAc) (puriss. p.a. ACS, Reag. Ph.
Eur., Reag. ISO) and dichloromethane (DCM) (puriss., meets analytical specification of Ph. Eur., NF,
≥99% GC) were supplied by Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Methanol
(MeOH) (≥99.7% purity) was purchased by Honeywell Riedel-de Haën (Seelze, Germany). Ultrapure
water from a Millipore Milli-Q Element A10 Water Purification System (Merck-Millipore, Milan,
Italy) was used during the experimental procedure.

Intermediate stock solutions of native and deuterated PAHs, each at 1 mg L⁻¹, were prepared in
methanol. Daily, standard native and deuterated PAHs working solutions were prepared by proper
dilution of the stock solutions before use.

134 2.2. Environmental snow sample collection

Surface snow samples collected on the coastal area of Victoria Land (Antarctica) during the 2020 –
2021 austral summer were kindly provided by the National Antarctic Research Program (PNRA).
Samples were maintained at -20°C until analysis, then they were thawed in the laboratory at room
temperature preventing exposure to solar irradiation and subjected to MEPS procedure.

139 2.3. Semi-automated MEPS procedure

140 The hand-held digital device eVol[®] Sample Dispensing System, the XCHANGE[®] enabled analytical

syringe (50 μ L), the Barrel Insert and Needle assemblies (BIN) packed with 4 mg of three different

silica-based sorbents (C2, C8 and C18), respectively were from SGE Analytical Science (SGE

143 Analytical Science Pty Ltd., Victoria, Australia).

144 Prior to first use, each BIN was activated three times with 50 µL of methanol followed by the same

145 volume of ultrapure water at a speed of 10 μ L s⁻¹.

Before the microextraction procedure, all glassware was rinsed three times with ultrapure hexane in order to avoid residues of organic contaminants (Arcoleo et al., 2020), as recommended when determining hydrophobic compounds (Giorio et al., 2018).

The sample (4 mL) was extracted from a 10 mL glass vial by 80 loading steps of 50 μ L each at a speed of 12.50 μ L s⁻¹ and all portions were discarded into the waste. Then the sorbent was dried by 10 cycles of pulling and pushing air at a flow rate of 25.00 μ L s⁻¹.

152 Considering that small aliquots commonly elute analytes of interest more efficiently than one large 153 aliquot (Beyer and Biziuk, 2010), the adsorbed PAHs were collected in three fractions (10 μ L each) 154 eluting with ethyl acetate at the speed of 1.67 μ L s⁻¹. The eluate was spiked with IS at the 155 concentration of 10 μ g L⁻¹ and 1 μ L of the solution was injected in the GC-MS. After the elution step 156 the sorbent was washed with ethyl acetate, methanol and ultrapure water (50 μ L each) to avoid any 157 carry-over and to condition the solid phase before the next extraction.

158 2.4. GC-MS analysis

The analysis of the 16 PAHs was performed using a HP 6890 Series Plus gas chromatograph (Agilent 159 Technologies, Milan, Italy) equipped with a PAL Combi-xt autosampler (CTC Analytics AG, 160 161 Switzerland) and coupled to a MSD 5973 mass spectrometer (Agilent Technologies). The S/SL (Agilent Technologies) injection port temperature was set at 300 °C and the gas chromatograph was 162 163 operated in the splitless injection mode. Separation was achieved on a Rxi-5Sil MS capillary column 164 (30 m x 0.25 mm i.d, 0.25 µm film thickness) (Restek, Bellefonte, PA, USA). Helium was used as carrier gas at a constant flow rate of 1.0 mL min⁻¹. The GC oven temperature program was set as 165 follows: 70 °C; 15 °C min⁻¹ to 290 °C (held for 4 min) for a total run time of 19.17 min. The mass 166 167 spectrometer was operated with an electron ionization (EI) ion source using an electron energy of 70 eV. A solvent delay time of 3.90 min was applied. The transfer line was maintained at 280 °C and the 168 ion source at 150 °C. 169

Preliminarily, the full scan mass spectral data were recorded in the 40–400 amu range (scan time: 2 scan s⁻¹) to select a list of both qualifier and quantifier ions per target analyte prior to analysis by GC-MS under selected ion monitoring (SIM) conditions. The SIM mode was used for quantitative measurements with a dwell time of 30 ms for each ion. The selected ions are listed in Table 1. The ChemStation (Agilent Technologies) was used for signal acquisition and data processing.

Table 1

Retention times and ions monitored for target PAHs (quantifier ions are underlined) in SIM mode.

PAHs	Retention time (min)	Qualifier and quantifier ions (m/z)
Nap-d8	4.40	<u>136</u> , 137, 108
Nap	4.43	<u>128</u> , 127, 102
Acy-d8	6.80	<u>160,</u> 158, 161
Acy	6.82	<u>152</u> , 151, 76
Ace-d10	7.04	<u>162</u> , 164, 160
Ace	7.09	<u>153</u> , 154, 76
Flu-d10	7.89	<u>176</u> , 174, 175
Flu	7.91	<u>166</u> , 165, 139
Phe-d10	9.41	<u>188</u> , 189, 184
Phe	9.45	<u>178</u> , 176, 152
Ant-d10	9.49	<u>188</u> , 189, 184
Ant	9.51	<u>178,</u> 176, 152
Flt-d10	11.27	<u>212</u> , 208, 213
Flt	11.30	<u>202</u> , 200, 101
Py-d10	11.61	<u>212</u> , 211, 208
Ру	11.64	<u>202</u> , 200, 101
BaA-d12	13.54	<u>240,</u> 236, 241
BaA	13.57	<u>228,</u> 226, 113
Chr-d12	13.59	<u>240,</u> 236, 241
Chr	13.62	<u>228,</u> 226, 113
BbF-d12	15.14	<u>264,</u> 265, 260
BbF	15.17	<u>252,</u> 253, 126
BkF-d12	15.18	<u>264,</u> 265, 263
BkF	15.21	<u>252,</u> 253, 126
BaP-d12	15.60	<u>264,</u> 265, 260
BaP	15.64	<u>252,</u> 253, 126
InPy-d12	17.59	<u>288</u> , 289, 144
DiahA-d14	17.65	<u>292,</u> 288, 293
InPy	17.64	<u>276</u> , 279, 278, 277, 139
DiahA	17.72	<u>278</u> , 279, 277, 276, 139
BghiP-d12	18.13	<u>288</u> , 287, 289
BghiP	18.19	<u>276</u> , 279, 278, 277, 139

175 2.5. Sorbent and elution solvent selection

The method was developed using uncontaminated snow from Antarctic Plateau as blank matrix after verifying in the chromatogram the absence of detectable signals attributable to the analytes (Fig. S1). Three reversed-phase sorbent materials (silica-C2, silica-C8 and silica-C18) were evaluated and compared for the enrichment of the target PAHs from water samples. For each sorbent the extraction of three independent replicate sample solutions spiked with PAHs at 500 ng L⁻¹ was performed.

181 After the optimization of best sorbent material, the effect of three different elution solvents 182 (dichloromethane, ethyl acetate and methanol) on PAHs desorption was investigated performing 183 extraction of three independent sample solutions spiked with PAHs at 250 ng L^{-1} for each solvent.

184 The performance of the sorbents and the elution solvents was expressed in terms of the relative 185 chromatographic peak areas using the formula:

186 Area ratio = A(spike, net)/A(internal standard)

where: A(spike, net) is the net chromatographic peak area of the compound in a spiked "blank"
sample which was subjected to MEPS; A(internal standard) is the chromatographic peak area of the
internal standard added after sample extraction.

190 2.6. *Optimization of the MEPS procedure by experimental design*

For optimization of experimental parameters, measurements were carried out on blank water derived from uncontaminated snow spiked with PAHs mixture at 250 ng L⁻¹. The influence of two factors on MEPS performance was studied using a face centred design (FCD). The investigated factors were the following: the number of loading cycles (x_1) and the number of eluting cycles (x_2). Low and high levels were: x_1 =40-80, x_2 =3-10.

This experimental plan allows the simultaneous investigation of the effects of the selected variables and of their interactions (Bianchi and Careri, 2008). Four replicates at the centre point were considered in the model to estimate the experimental variability. The FCD was used to calculate the final regression models which were used to identify the optimal conditions by means of the multicriteria method of the desirability functions (Vera Candioti et al., 2014). The software package
SPSS Statistics 23.0 (IBM, Milano, Italy) was used for statistical calculations.

202 2.7. Analytical validation

Method validation was performed under the optimized conditions according to EURACHEM 203 guidelines (Magnusson and Örnemark, 2014). Uncontaminated snow from Antarctic Plateau was 204 used as blank samples. Limits of detection (y_D) and of quantification (y_O) were estimated as signals 205 by using the standard deviation (s_b) and the mean (x_b) calculated from 10 blank replicate 206 measurements as follows: $y_D = x_b + 3 s_b$ and $y_Q = x_b + 10 s_b$. The concentration values of the limit of 207 detection (LOD) and the limit of quantification (LOQ) were obtained by projecting the corresponding 208 responses y_D and y_Q against the concentration axis through a calibration plot y = f(x). Calibration 209 curves were constructed on six concentration levels in the LOQ-150 ng L⁻¹ range performing three 210 replicated measurements for each level. Mandel's fitting test was applied to assess the linearity and a 211 Student's *t*-test was used to establish the significance of the intercept (significance level 5%). 212 Repeatability and intermediate precision over three days were calculated in terms of RSD% 213 performing six measurements on three concentration levels (15, 50 and 150 ng L⁻¹), respectively. 214 Trueness in terms of recovery rate (RR%) was evaluated carrying out ten replicated measurements at 215 20, 70 and 130 ng L^{-1} , respectively, and calculated as follows: 216

$$RR\% = \frac{c_1}{c_2} \times 100$$

where c_1 is the measured concentration and c_2 is the concentration determined from the amount spiked in the sample.

220 Before each injection, IS was added at 10 μ g L⁻¹ to the PAH standard solutions and to samples after 221 extraction.

222 2.8. Enrichment factors

The enrichment capabilities of semi-automated MEPS-C8 were evaluated in terms of enrichment factors (EFs). Under the optimized conditions, EFs were calculated as the ratio of the concentration of the analytes at 20 and 50 ng L⁻¹ extracted by MEPS to that obtained by the direct injection of 1 μ L of standard solution of PAHs at 10 μ g L⁻¹. Experimentally, the ratio of the chromatographic peak area for each analyte after MEPS was compared to that obtained by direct injection and corrected by using the proper response factor (Riboni et al., 2016). Three replicate measurements were carried out.

229 3. Results and discussion

230 *3.1. Development of MEPS procedure*

In the present study, MEPS was carried out using the "extract-discard" procedure, which consists in 231 232 discarding each sample portion into the waste after the aspiration step. Differently, in the "draw-eject" 233 mode the sample is aspirated and dispensed in the same vial several times. According to previous studies (Prieto et al., 2010; Quinto et al., 2014), the "extract-discard" mode was selected to obtain 234 235 better performances in terms of recovery and sensitivity. In fact, Prieto et al., 2010, 2011) demonstrated that by using the "extract-discard" mode, it is possible to achieve similar or higher 236 responses than those achieved with the multiple draw-eject procedure. In addition, by applying this 237 extraction mode a reduction of the mechanical stress of the MEPS syringe plunger can be obtained, 238 239 thus improving MEPS syringe lifetime.

Important parameters affecting MEPS efficiency, such as type of sorbent material and type of elution solvent (Fu et al., 2012; Pereira et al., 2014; Yang et al., 2017) were investigated. A washing step usually recommended between sample loading and elution step to remove matrix unwanted substances (Abdel-Rehim, 2011) was not applied, since the chromatogram of the blank matrix showed the absence of peaks related to the presence of interferences (Fig. S1). In addition, it should be considered that the use of washing solution could affect analyte recovery (El- Beqqali et al., 2007).

Preliminarily, sample loading speed and analyte elution speed were evaluated considering the 246 247 processing time *per* sample combined with the efficiency of analyte sorption and partition (Mendes et al., 2012) and subsequent desorption process (data not shown). Taking into account the speed range 248 available on the eVol[®] device provided with a 50 µL syringe, i.e., 1.67-25.00 µL s⁻¹, extraction and 249 elution rates were found to be appropriate operating at 12.50 μ L s⁻¹ and 1.67 μ L s⁻¹, respectively. As 250 suggested by Abdel-Rehim (Abdel-Rehim, 2011), extraction speed in the range of 10-20 µL s⁻¹ is 251 suitable for maximizing the interactions between analytes and sorbent, thus improving the retention 252 capability of the MEPS technique. As for the elution rate, the use of the lowest speed enables a good 253 analyte elution as well as the use of a reduced solvent volume. In addition, it should be considered 254 255 that by operating under the selected conditions, it was possible to prevent bubbling in the syringe, thus improving method repeatability. Similar results were also reported by Prieto et al. (Prieto et al., 256 2010) which obtained optimal performance for the extraction of organic compounds including PAHs 257 when the fill and injection speed had intermediate and low values, respectively. 258

259 3.1.1. Comparison of performance of different silica-based sorbents on PAH microextraction

260 Up to date, numerous sorbents have been studied with the MEPS technique based not only on the 261 nature of the analytes, but also accounting for the sample matrix in order to achieve adequate recovery (Moeder et al., 2010; Prieto et al., 2011; Pereira et al., 2014; Moein et al. 2015; Fernández et al., 262 263 2017; Yang et al., 2017). In this study, selectivity towards target PAHs was assessed by evaluating the extraction capability of three different types of sorbent materials packed in the MEPS BIN. Silica-264 265 based reversed-phase sorbent materials are suitable for the extraction of lipophilic compounds from aqueous matrix (Yang et al., 2017). In this context, a comparative evaluation of the efficiency of the 266 C2, C8 and C18 sorbent phases for the enrichment of the analytes from water samples was carried 267 268 out. In this first investigation step, dichloromethane was used as eluting solvent since previous studies reported its high elution efficiency for the determination of PAHs in water samples (Ma et al., 2010; 269

Fu et al., 2012; Paszkiewicz et al., 2018). Afterwards, the effect of other elution solvents on extraction
recovery was evaluated for the selected sorbent phase.

Fig. 1 shows that C8-BIN exhibited better performance for most of the analytes, particularly for two, 272 three- and four-ring PAHs due to the highest sorption/partition capacity, whereas for InPy, DiahA 273 and BghiP the highest yield was achieved using C2-BIN. This behaviour could be explained taking 274 into account the stronger retention of the heaviest PAHs on the C8 sorbent compared to C2, revealing 275 276 a less effective elution process. By contrast, C18-BIN showed the lowest yield for PAHs with fouror more aromatic rings. This result is consistent with the non-polar nature of C18 phase characterized 277 by the presence of longer alkyl chain, providing stronger retention of more hydrophobic compounds 278 279 and then poor recovery when eluting with reduced solvent volume (Oleszczuk and Baran, 2004; Buszewska-Forajta et al., 2018). Taking into account a wide range of log Kow values of the herein 280 considered analytes (ranging from 3.30 (naphthalene) to 6.95 (indeno[1,2,3-cd]pyrene) (Miller et al., 281 282 1984), C8-BIN is proposed as a most suitable MEPS sorbent material being characterized by a more balanced performance for this application than C2-BIN and C18-BIN. 283



284

Fig. 1 Comparison of extraction efficiency of the MEPS C2-BIN, C8-BIN and C18-BIN sorbents. Sample spiked concentration, 500 ng L⁻¹; pump cycles of sample loading, $40 \times 50 \mu$ L; speed of sample loading, 12.50

287 μ L s⁻¹; pump cycles of eluent, 10 × 10 μ L; elution solvent, dichloromethane; speed of elution solvent; 1.67 μ L 288 s⁻¹.

289 3.1.2. Comparison of performance of different desorption solvents on PAH microextraction

The type of elution solvent is a further parameter affecting the performance of MEPS (Moein et al., 290 2015). The effect of DCM, EtAc and MeOH was studied for the elution of the 16 PAHs from C8-291 292 BIN performing three independent replicate experiments for each solvent. As shown in Fig. 2, the best recovery for all target analytes except for Nap was observed when using EtAc. The lowest 293 294 response obtained by DCM could be ascribed to residual water on the sorbent particles packed in the BIN after sample loading despite the drying step, thus resulting in an unsatisfactory recovery of PAHs 295 being DCM immiscible with water. MeOH has been previously reported as elution solvent in MEPS 296 procedures for PAH extraction using silica-based sorbents (El-Beqqali et al., 2006; Fu et al., 2012; 297 298 Quinto et al., 2012, 2014). However, in our study MeOH responses were lower than EtAc except for naphthalene, which presents the lowest octanol/water partition coefficient (K_{ow}) (Miller et al., 1984), 299 300 thus facilitating its desorption by using MeOH. The effect of solvents was tested carrying out a oneway ANOVA followed by Bonferroni t-test for multiple comparisons. ANOVA highlighted the 301 presence of significant differences (p < 0.05) between mean responses. Afterwards, *t*-test revealed 302 303 that EtAc exhibited similar or higher extraction yield (p < 0.05) (except for Nap) compared to MeOH. On the basis of these findings, EtAc was used as elution solvent. 304

Fig. 2 Comparison of extraction efficiency as a function of elution solvent (DCM, EtAc, MeOH). Sample spiked concentration, 250 ng L⁻¹; pump cycles of sample loading, $40 \times 50 \mu$ L; speed of sample loading, 12.50 μ L s⁻¹; pump cycles of eluent, $10 \times 10 \mu$ L; type of BIN, C8; speed of elution solvent; 1.67 μ L s⁻¹.

309 3.2. Microextraction optimization by experimental design

310 Once the loading and elution speeds were adjusted and after the selection of sorbent and elution 311 solvent, the number of both loading and elution cycles were optimized using a FCD.

312 As for the number of loading cycles, ideally the proper concentration factor for the analytes should

be achieved with a reduced number of loading cycles to avoid long extraction times (Pereira et al.,

2014). The calculated regression models used to estimate the optimal extraction conditions for the 16

- BAHs are shown in Table 2. The variable x_1 , when significant, indicates an increase in the GC-MS
- response of PAHs in correspondence to a high number of loading cycles, whereas a reduced number
- 317 of elution steps is suitable to obtain a satisfactory recovery.
- 318

305

319 **Table 2**

320 Regression coefficients of the polynomial functions calculated by optimization procedure.

PAHs Regression models

	201
Nap	$y = 574 (\pm 30) + 118 (\pm 39)x_1 - 230 (\pm 39)x_2$
Acy	$y = 666 \ (\pm \ 34) + 104 \ (\pm \ 43) x_1 - 283 \ (\pm \ 43) x_2$
Ace	$y = 499 \ (\pm \ 27) + 96 \ (\pm \ 34) x_1 - 200 \ (\pm \ 34) x_2$
Flu	$y = 569 \ (\pm \ 32) + 111 \ (\pm \ 40) x_1 - 240 \ (\pm \ 40) x_2$
Phe	$y = 848 \ (\pm \ 50) + 152 \ (\pm \ 64) x_1 - 375 \ (\pm \ 64) x_2$
Ant	$y = 640 \; (\pm \; 41) + 122 \; (\pm \; 51) x_1 - 296 \; (\pm \; 51) x_2$
Flt	$y = 798 \; (\pm 46) + 145 \; (\pm 58) x_1 - 359 \; (\pm 58) x_2$
Ру	$y = 819 \ (\pm \ 46) + 138 \ (\pm \ 58) x_1 - 350 \ (\pm \ 58) x_2$
BaA	$y = 489 \ (\pm \ 34) - 193 \ (\pm \ 43) x_2$
Chr	$y = 495 \ (\pm \ 34) - 199 \ (\pm \ 43) x_2$
BbF	$y = 304 \ (\pm \ 28) + 74 \ (\pm \ 35) x_1 - 198 \ (\pm \ 35) x_2$
BkF	$y = 301 \ (\pm \ 28) + 74 \ (\pm \ 35) x_1 - 173 \ (\pm \ 35) x_2$
BaP	$y = 325 \ (\pm \ 34) - 181 \ (\pm \ 43) x_2$
InPy	$y = 201 \ (\pm \ 23) - 204 \ (\pm \ 29) x_2$
DiahA	$y = 133 \ (\pm \ 25) - 159 \ (\pm \ 31) x_2$
BghiP	$y = 212 \ (\pm \ 23) - 216 \ (\pm \ 29) x_2$

322 $\overline{x_1: \text{ number of loading cycles.}}$

323 x₂: number of elution cycles.

Finally, the optimal conditions for the simultaneous extraction of the investigated PAHs were identified by using the multicriteria method of desirability functions, resulting in 80 loading cycles and 3 elution cycles. The developed procedure achieved a global desirability D = 0.91 and good single desirability values always higher than 0.9, proving method feasibility for the simultaneous extraction of the target analytes. The method can be considered also time efficient with an average time of 20 min *per* sample if compared to previously reported MEPS procedures, requiring a higher number of loading and elution cycles. (Quinto et al., 2012, 2014).

331 *3.3.* Analytical performance of the MEPS-GC-MS method

The validation parameters such as linearity, LOD, LOQ, trueness and precision were evaluated for the GC-MS determination of the 16 target PAHs under the above-mentioned optimal extraction conditions. Enrichment factors were also calculated to assess the extraction capabilities of the C8 sorbent, obtaining good EFs values ranging from 64 (\pm 7) for Ace to 129 (\pm 18) for Phe. For confirmation purposes, EFs were also calculated using a concentration of 20 ng L⁻¹, obtaining results comparable with those calculated using a concentration of 50 ng L⁻¹.

As shown in Table 3, the developed method achieved excellent LOD values at the low ng L^{-1} level 338 339 for all the target compounds, demonstrating its capability for the analysis of PAHs at ultra-trace levels. These values are comparable with those reported in previous studies (Quinto et al., 2012, 340 2014), which validated the MEPS-based method on spiked ultrapure water. Good linearity was 341 verified by applying Mandel's fitting test in the $LOQ - 150 \text{ ng } \text{L}^{-1}$ range for all the analytes. Precision 342 studies showed RSDs% for repeatability in the 0.3–11% range at the lowest concentration (15 ng L⁻ 343 ¹) and in the 0.1–10% range at the highest concentration level (150 ng L⁻¹). As for intermediate 344 precision, RSD values always lower than 15% were found (Table S1). Recovery rates in the 77.6 (\pm 345 0.1)-120.8 (\pm 0.1)% range (n = 10) were obtained (Table S2), thus proving good trueness of the 346 developed method. The selectivity of the method was also evaluated testing the absence of interfering 347 peaks at the retention times of the target PAHs when analyzing a blank sample and a snow sample, 348 349 as shown in Figs. S1 and S3.

350 Similarly to Quinto et al. (Quinto et al., 2012, 2014), the present method was developed, optimized and validated for the determination of very diverse chemical compounds with a wide range of physical 351 352 and chemical properties, whereas other MEPS procedures only concerned low-molecular weight PAHs (El-Beggali et al., 2006; Fu et al., 2012) (Table 4). In addition, the achieved LODs were 353 obtained by extracting low sample volume, i.e. 4 mL, representing a further improvement in temporal 354 resolution records compared to other studies on PAHs contamination in polar sites using very large 355 sample volume (7 – 10 L) (Fuoco et al., 2012; Vecchiato et al., 2015). Finally, the herein described 356 method revealed advantageous due to the use of a commercially available and cost-effective sorbent 357 phase that could be reused more than 300 times. 358

359 **Table 3**

360 Analytical parameter	rs of the MEPS-GC-MS method.
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PAHs	LOD (ng L ⁻¹)	LOQ (ng L ⁻¹)	$b_0(\pm s_{b_0})$	$b_1(\pm s_{b_1})$
Nap Acy Ace Flu	1.1 1.3 1.4 0.7	3.6 4.3 4.7 2.4	0.088 (± 0.003) 0.026 (± 0.005) - 0.03 (± 0.01)	0.00248 (± 0.00004) 0.0023 (± 0.0001) 0.0036 (± 0.0001) 0.0027 (± 0.0001)

Phe	0.3	1.1	0.17 (± 0.01)	$0.0029 (\pm 0.0001)$
Ant	1.3	4.2	$0.07~(\pm 0.01)$	$0.0030 (\pm 0.0001)$
Flt	0.3	1.1	0.05 (± 0.01)	$0.0039 (\pm 0.0002)$
Py	0.4	1.4	$0.06 (\pm 0.02)$	$0.0044 \ (\pm 0.0002)$
BaA	0.6	1.9	$0.04~(\pm 0.01)$	0.0036 (± 0.0001)
Chr	0.5	1.7	$0.04~(\pm 0.01)$	0.0061 (± 0.0001)
BbF	2.5	8.4	0.06 (± 0.02)	$0.0032 (\pm 0.0002)$
BkF	2.5	8.3	-	$0.0064 \ (\pm 0.0002)$
BaP	3.8	12.5	0.09 (± 0.02)	$0.0040 (\pm 0.0003)$
InPy	3.5	11.5	0.05 (± 0.01)	$0.0034 (\pm 0.0001)$
DiahA	4.6	15.3	-	$0.0042 (\pm 0.0001)$
BghiP	4.2	13.9	0.07 (0.02)	$0.0037 (\pm 0.0002)$

361 Calibration curve equation: $y = b_0 + b_1 x$.

362 (-): intercept not statistically significant.

363 Table 4

364 Comparison of the developed method with other MEPS methods for the determination of PAHs.

Analytes	Extraction mode	Sorbent material	Sample loading condition ^a	Elution condition ^a	LOQ (ng L ¹)	Technique	Reference
5 PAHs	Draw-eject	C8	60 × 50 μL (20 μL s ⁻¹)	1 × 30 μL (20 μL s ⁻¹)	5	GC-MS	El-Beqqali et al. (2006)
8 PAHs	Draw-eject	C18	40 × 50 μL (5 μL s ⁻¹)	1 × 50 μL (3 μL s ⁻¹)	2.5 - 27.5	GC-MS	Fu et al. (2012)
16 PAHs	Draw-eject	C8	300 × 50 μL (1.67 μL s ⁻¹)	20 × 50 μL (1.67 μL s ⁻¹)	1.6 - 6.2	GC-MS	Quinto et al. (2012)
16 PAHs	Extract- Discard	C8	90 × 50 μL (4 μL s ⁻¹)	1 × 50 μL (4 μL s ⁻¹)	0.8 - 2.0	GC-MS	Quinto et al. (2014)
16 PAHs	Extract- Discard	C8	80 × 50 μL (12.50 μL s ⁻¹)	3 × 10 μL (1.67 μL s ⁻¹)	1.1 – 15.3	GC-MS	This work

365 ^a Number of pulled/pushed cycles × aspirated volume (speed)

366 *3.4.* Applicability of the MEPS-GC-MS method to the analysis of Antarctic snow samples

The applicability of the developed method was proven by carrying out the determination of PAHs in five surface snow samples kindly provided by PNRA and collected during the 2020 – 2021 austral summer in Antarctica at four sites on the coast of Victoria Land (Fig. 3). Sample A was collected nearby the meteorological station of Icaro Camp (74°42'37" S, 164°07'05" E); samples B and E were from the area of the scientific research base "Enigma Lake" (74°43' S, 164°01' E); samples C and D were collected near Cape Phillips (73°03' S, 169°36' E) and Adélie Cove (74°45' S, 164°00' E), respectively. The latter is a colony of about 13 - 15 thousand nests of Adélie penguins.

As shown in Table 5, PAHs with more than four aromatic rings were not detected in the investigated 374 375 samples. This could be ascribed to the low presence of high-molecular weight PAHs in snow matrix being more lipophilic and less water soluble than lighter PAHs (Korosi et al., 2015). The covered 376 Σ_{16} PAHs concentrations for each sample revealed values ranging from 24 to 39 ng L⁻¹, with the lowest 377 concentration detected at site D corresponding to Adélie Cove. However, among the different sites 378 379 considered, comparable Σ_{16} PAHs concentrations were observed, even for the most distant located area (Cape Phillips). Nap and Flu presented the highest concentration level compared to the other 380 analytes in all sampling sites (41 and 42% of the total Σ_{16} PAHs, respectively). Nap and Flu are main 381 components of diesel fuel (Dandajeh et al., 2019), therefore our results are in agreement with other 382 383 studies describing the presence of regional environmental pollution around scientific stations due to ship operations and fuel combustion (Bargagli, 2008; Kukučka et al., 2010; Vecchiato et al., 2015). 384 In addition, the total Σ_{16} PAHs concentration found in the analysed samples is 158 ng L⁻¹, very similar 385 386 to that achieved by Vecchiato et al. (Vecchiato et al., 2015) who attributed the major contribution to the anomalous Nap concentration detected in the sample collected at Mid Point, assuming a possible 387 PAH distribution by the wind from a twin-otter refueling point. These considerations support the 388 hypothesis of PAHs contamination influenced by local sources. 389

In general, it can be stated that Antarctic contamination level for PAHs is low compared to other 390 391 remote areas. For a frame of reference, the found PAH concentrations were compared to those determined in other remote areas, e.g. Caucasus and Alps. Vecchiato et al. (Vecchiato et al., 2020) 392 measured PAHs concentrations in the ice core drilled in 2009 at the western plateau of Elbrus 393 obtaining the most recent Elbrus PAH concentrations at the top of the core in the 112 - 166 ng L⁻¹ 394 395 range. Gabrieli et al. (Gabrieli et al., 2010b) examined the seasonal snowpack from Eastern Italian Alps in 2004-2005. Σ PAHs concentration in high altitude sites (>1700 m a.s.l.) was in the 20 – 59 ng 396 L^{-1} range. The highest Σ PAHs concentration was 290 ng L^{-1} in valley bottom urban area. Finally, 397 when comparing different remote environments it should be noted that the differences of 398

399 contamination level reflect the influence for each sampling site of their regional sources as well as

the deposition regime and the emission pattern of PAHs. 400

401 Table 5

402 Concentrations of PAHs detected in the Antarctic snow samples

PAHs	Icaro (A)	Enigma (B)	Cape Phillips (C)	Adélie Cove (D)	Enigma2 (E)
Nap	11.2	8.8	7.8	6.7	6.0
Acy	n.d.	n.d.	7.1	n.d.	7.4
Ace	n.d.	n.d.	n.d.	n.d.	n.d.
Flu	10.1	7.8	8.1	7.7	8.5
Phe	n.d.	n.d.	n.d.	n.d.	n.d.
Ant	n.d.	n.d.	n.d.	n.d.	n.d.
Flt	5.2	6.2	5.2	5.1	5.3
Ру	4.3	5.7	4.2	4.4	4.2
BaA	n.d.	6.9	n.d.	n.d.	n.d.
Chr	n.d.	3.5	n.d.	n.d.	n.d.
BbF	n.d.	n.d.	n.d.	n.d.	n.d.
BkF	n.d.	n.d.	n.d.	n.d.	n.d.
BaP	n.d.	n.d.	n.d.	n.d.	n.d.
InPy	n.d.	n.d.	n.d.	n.d.	n.d.
DiahA	n.d.	n.d.	n.d.	n.d.	n.d.
BghiP	n.d.	n.d.	n.d.	n.d.	n.d.

403 404 All data in ng L⁻¹. n.d.: not detected.

405 406

Fig. 3 Sampling sites of surface snow in Antarctica

407 4. Conclusions

An eco-friendly semi-automated MEPS-GC-MS method was successfully devised, validated and 408 409 applied for the first time to the extraction of the 16 US-EPA priority PAHs from Antarctic snow samples at ultra-trace levels. The optimized method based on the use of silica-C8 sorbent exhibited 410 411 high extraction efficiency allowing highly sensitive analysis of environmentally important PAHs in snow samples. The semi-automatic sample preparation provided high precision and reduced sample 412 handling avoiding potential contamination during the extraction procedure. An additional advantage 413 of the proposed method relies on the reduced sample volume, representing a promising tool to meet 414 challenges of high temporal resolution records in paleoclimatic investigations. 415

The optimized method proved to be suitable for ultra-trace analysis of PAHs in snow samplescollected in four sites in Antarctica revealing a likely contribution of local pollution sources to PAHs

418 contamination of Antarctic environment. Future applications of the developed MEPS method for 419 ultra-trace analysis of PAHs in snow/firn and ice cores from polar regions could provide 420 paleoenvironmental records in order to assess the occurrence and global contamination with PAHs 421 and other emerging contaminants.

422

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