

1 **Evaluation of uncertainty associated to determination of particle-**
2 **bound PAHs in ambient air by TD-GC/MS and Soxhlet-GC/MS.**

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4 **Iñaki Elorduy^{*}, Nieves Durana, José Antonio García, María Carmen Gómez,**
5 **Lucio Alonso**

6
7 *Chemical and Environmental Engineering Department, School of Engineering, University of the*
8 *Basque Country, Alameda de Urquijo s/n, E-48013, Bilbao, Spain*

9
10 **Abstract**

11
12 The knowledge of the uncertainty associated to an analytical method is necessary to evaluate the
13 quality of the results measured by itself. In this work the uncertainty associated to analytical
14 measurement of polycyclic aromatic compounds (PAHs) in ambient air by thermal desorption
15 coupled with gas chromatography-mass spectrometry (TD-GC/MS) was evaluated. The study
16 was focused on analyses of particulate phase (PM₁₀) and the results were compared to those
17 obtained a conventional solvent extraction (Soxhlet-GC/MS). The main sources for combined
18 uncertainty were calibration curve, recovery of the extraction stage, area or volume of sample and
19 volume of air. The TD-GC/MS reported lower combined uncertainty (<10 %) than Soxhlet-
20 GC/MS (values between 11 and 18 %) for measurement of particle-bound PAHs in air. The major
21 uncertainty contributions resulted from the recovery of each analyzed PAH and the calibration
22 curves.

23
24 **Keywords:** Uncertainty; PAHs; Thermal desorption; Soxhlet extraction; GC-MS; PM₁₀ samples.

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*Corresponding author: Tel.:+34 946017297.

E-mail: inaki.elorduy@ehu.eus

32 INTRODUCTION

33

34

35 Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds containing only
36 carbon and hydrogen atoms, constituted by two or more condensed aromatic rings. These
37 substances are generated by all incomplete combustion processes of organic material, being the
38 anthropogenic activities their major sources (Ravindra *et al.*, 2008).

39 PAHs have aroused global concern due to their high persistence within the environment and their
40 adverse health effects. As result of this, several international agencies have listed PAHs as
41 priority pollutants (US-EPA, 1982; ATSDR, 1995; WHO, 1998). Although the analysis of PAHs
42 in air is of considerable importance for air quality assessment, PAH data in air is still scarce, and
43 most of the studies show large spatial and temporal uncertainties due to the complex sampling
44 and analytical procedures required.

45 The environmental samples of PAHs can be difficult to analyze due to their complexity (multi-
46 phase and multi-component samples in very low concentrations). For this reason, a solvent
47 extraction and pre-concentration technique in combination with a chromatographic method
48 (liquid and/or gas chromatography) is the most frequently used methodology for the
49 determination of PAHs (US-EPA, 1999; ISO 12884:2000; ISO 16362:2005; Poster *et al.*, 2006).

50 Conventional sample preparation methods involve several steps leading to the possibility of loss
51 or contamination. Since PAH concentrations in ambient air are low, it is essential to reduce the
52 number of pretreatment steps and the solvent volume in order to reduce the level of blank
53 contamination and the risk of losing analytes by evaporation in the concentration steps (Delgado-
54 Saborit, 2010). Among the solvent extraction and pre-concentration techniques, thermal
55 desorption (TD) provides advantages that overcomes the main drawbacks of the conventional
56 solvent extractions (Van Drooge *et al.*, 2009). The features of this technique (the absence of

57 sample manipulation, high desorption efficiency, good sensitivity and reproducibility, elimination
58 of interferences, and lower extraction times and costs) provide a faster, simpler, and more
59 sensitive and accurate method to determine trace level PAHs in ambient air (Kim and Kim, 2015).
60 TD technique coupled with gas chromatography/mass spectrometry (GC/MS) has been mainly
61 applied for the analysis of particle-bound PAHs (Bates *et al.*, 2008; Gil-Molto *et al.*, 2009; Van
62 Drooge *et al.*, 2009).

63 According to the international standard (ISO 20988:2007) the uncertainty of a measurement is
64 defined as “a parameter associated with the result of a measurement that characterizes the
65 dispersion of the values that could reasonably be attributed to the measurand”. Estimation of
66 uncertainty leads to better measurement reliability, renders data from inter-laboratory studies
67 comparable, and helps to assess the statistical significance of the difference between the
68 measurement and a relevant reference value. In case of regulated pollutants such as PAHs, the
69 measurement uncertainty is necessary to evaluate the quality of the results and for their proper
70 interpretation.

71 The aim of this study was to evaluate the major uncertainty contributions associated with the
72 determination of particle-bound PAHs in air samples by an analytical method based on TD-
73 GC/MS. This technique has been previously optimized and applied to determinate these
74 compounds in real 8h-samples (PM₁₀) (Elorduy *et al.*, 2016). Furthermore, the uncertainties
75 associated with the conventional analytical method (Soxhlet-GC/MS) were also determinate in
76 order to compare the reliability of measurements obtained from each method. One important
77 contribution of this work is that there are few studies in the literature that provide a
78 comprehensive evaluation of the uncertainty derived from the determination of PAHs by TD
79 technique.

80

81 **Experimental**

82

83 ***Reagents and materials***

84 The PAH standards used were SV Calibration Mix 5 from Restek Corporation (Bellefonte, PA,
85 USA) containing 2000 $\mu\text{g mL}^{-1}$ of naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace),
86 fluorene (FL), phenanthrene (Phe), anthracene (Ant), fluoranthene (Ft), pyrene (Pyr),
87 benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene, (BbFt), benzo[k]fluoranthene
88 (BkFt), benzo[a]pyrene, (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBahA),
89 and benzo[ghi]perylene (BghiP) in methylene chloride.

90 The pre-deuterated PAHs used were naphthalene- d_8 (Naph- d_8), biphenyl- d_{10} (Biph- d_{10}),
91 phenanthrene- d_{10} (Phe- d_{10}), pyrene- d_{10} (Pyr- d_{10}), benzo[a]anthracene- d_{12} (BaA- d_{12}),
92 benzo[a]pyrene- d_{10} (BaP- d_{10}) and benzo[ghi]perylene- d_{12} (BghiP- d_{12}), from Chiron (PAH
93 Mixture 6, Trondheim, Norway), 200 $\mu\text{g mL}^{-1}$ in toluene.

94 Decafluorobiphenyl, 4,4'-dibromooctafluorobiphenyl, 4,4'-dibromobiphenyl (Restek, 2000 μg
95 mL^{-1} in methylene chloride) and indeno[1,2,3-cd]pyrene- d_{12} (Chiron, 100 $\mu\text{g mL}^{-1}$ in toluene)
96 were used as recovery standard for the assessment of Soxhlet extraction efficiency.

97 Solutions were prepared by appropriate dilution in methanol HPLC grade (99.9 %, Lab-Scan
98 Analytical Sciences, Poland).

99 Standard Reference Material (SRM) 1649b urban dust, obtained from the National Institute of
100 Standards and Technology (NIST, Gaithersburg, MD, USA) was used in the validation of the
101 analytical methods.

102

103 ***Sample collection***

104 Airborne particulate matter (PM_{10}) samples were collected on pre-heated (at 500 °C for 24 h)
105 quartz fiber filters (150 mm diameter, Whatman International Ltd., United Kingdom) using a

106 high volume sampler (Digital DHA-80, Digital Elektronik AG, Switzerland) with a flow rate of
107 $30 \text{ m}^3 \text{ h}^{-1}$. After sampling, the filters were put into individual Petri dishes, wrapped in aluminum
108 foil, and kept in a $4 \text{ }^\circ\text{C}$ freezer until analysis (<15 days) according to ISO 12884:2000.

109

110 *Analytical procedure*

111 *TD-GC/MS*

112 Each loaded filter were randomly cut into 8 portions of 1 cm^2 and introduced into stainless-steel
113 tubes (90 mm length \times 6 mm o.d. \times 5 mm i.d., Perkin Elmer S.L., Spain). This was performed in
114 the same way as other studies (Ringuet *et al.*, 2012; Grandesso *et al.*, 2013), which demonstrated
115 good homogeneity results when using small sections of the filters. Before the analysis, the loaded
116 filters were spiked with $1 \text{ }\mu\text{L}$ of deuterated PAH solution ($20 \text{ ng } \mu\text{L}^{-1}$). Pre-heated ($500 \text{ }^\circ\text{C}$, 24 h)
117 silanized glass wool (Supelco Inc., Bellefonte, USA) was introduced at the end, and at the head
118 of the desorption tubes in order to prevent system contamination.

119 The analysis of the samples were performed using an automatic thermal desorption unit
120 (PerkinElmer Turbomatrix 150 ATD) coupled by a fused-silica capillary transfer line (0.32 mm
121 i.d.) to GC/MS (PerkinElmer Clarus 500). TD-GC/MS method was development and applied for
122 the measurement of particle-bound PAHs in ambient air (Elorduy *et al.*, 2016). The thermal
123 desorption was carried out in two stages. In the “primary desorption” stage, the sampling tubes
124 were placed into the desorption oven at ambient temperature. After a leak test and ambient
125 temperature purge by carrier gas (helium) to remove oxygen; the samples were thermally
126 desorbed at $350 \text{ }^\circ\text{C}$ for 10 min using a flow of inert gas (in this work, helium at 173 mL min^{-1}) to
127 extract analytes from the sample. These analytes were re-focused on a Peltier-cooled trap at -10
128 $^\circ\text{C}$. Once the primary desorption was complete, the trap was quickly heated until $325 \text{ }^\circ\text{C}$ for 6 min
129 (the “secondary desorption” stage). The trapped analytes were released and swept (by a helium
130 flow of 12 mL min^{-1}) through the heated transfer line (at $280 \text{ }^\circ\text{C}$) to the GC column.

131 The chromatographic separation of PAHs was conducted on a Meta.X5 (silphenylene phase)
132 capillary column: 30 m length x 0.25 mm i.d. x 0.25 mm film thickness (Teknokroma, Spain).
133 The helium gas carrier pressure employed in the GC/MS system was 21 psi and the column
134 temperature was programmed as follows: initial temperature 100 °C for 3 min, ramp of 10 °C
135 min⁻¹ until 250 °C, ramp of 5 °C min⁻¹ until 320 °C, and finally temperature held at 320 °C for 10
136 min. The total analysis time was 42 min per sample. The MS operated simultaneously in full scan
137 (SCAN) and selective ion monitoring (SIM) modes with the transfer line (from GC to MS) and
138 the source at 280 °C and 250 °C, respectively. Analytes were afterwards identified by comparing
139 their retention times and mass-to-charge ratios (m/z) with standards and literature data.

140

141 *Soxhlet-GC/MS*

142 The Soxhlet extraction was performed by Büchi extraction system B-811, an automated system
143 that can be used to perform an extraction according to the original Soxhlet principle. The loaded
144 filters (150 mm diameter) were extracted with hexane using the Soxhlet Warm mode. This mode
145 demonstrated advantages for reducing extraction time against conventional Soxhlet extraction in
146 previous works in our laboratory (Elcoroaristizabal *et al.* 2014), allowing an optimal extraction in
147 3hours.

148 Before the extraction, the loaded filter was spiked with 1 µL of a solution (0.5 ng µL⁻¹) of the
149 recovery standards.

150 After Soxhlet extraction process, the extracts of 5 mL were concentrated by a stream of dry
151 nitrogen to a volume less than 0.5 mL. Finally, these extracts were diluted to 1.5 mL with
152 methanol and 25 µL of a deuterated PAHs solution (20 ng µL⁻¹) were spiked.

153 2 µL aliquots from each extract were injected into the GC/MS with split mode. Table 1 collects
154 the timed events and the oven program used in the Soxhlet-GC/MS method.

155

156 **Table 1.** Timed events and oven program used in direct injector mode.

Timed event			Oven program			
Event	Flow (mL min ⁻¹)	Time (min)	Ramp	Rate (°C min ⁻¹)	Temperature (°C)	Hold (min)
Split	0	-0.51	Initial	0	45	1
Split	50	1	1	20	200	0
Split	20	5	2	4	320	5

157

158 Also, in this method, PAHs were identified based on their retention times and m/z value.

159

160 **Results and discussion**

161

162 **Validation**

163 The performance of both methods when applied to atmospheric PM samples was determined
 164 using and Standard Reference Material (SRM) 1649b urban dust. The repeatability and recovery
 165 of the method were calculated by adding known amounts of the SRM 1649b to blank quartz fiber
 166 filters (Whatman International Ltd, United Kingdom)

167 In TD-GC/MS method, 10.3±0.3 mg were weighted and deposited on one-eighth of a 47 mm
 168 diameter filters (n = 10), which were rolled and put into the desorption tubes. Silanized glass
 169 wool (Supelco Inc., Bellefonte, USA) was introduced at the end, and at the head of the desorption
 170 tubes in order to prevent system contamination.

171 In the case of Soxhlet-GC/MS method, 412.5±76.8 mg were deposited on one-eighth of a 150
 172 mm diameter filters (n = 7). Before the extraction, the loaded filter was spiked with 1 µL of a
 173 solution (0.5 ng µL⁻¹) of the recovery standards.

174 Prior to use, glass wool plugs and filters were heated at 350 °C for 24 h to remove trace organic
 175 compounds. Before the analysis, filters were spiked with a deuterated PAH internal standard
 176 solution (1 µL and 25 µL of 20 ng µL⁻¹ for TD and Soxhlet method, respectively).

177 Table 2 and 3 lists the results of the comparison between the calculated concentrations and the
 178 certificate values obtained for each PAH and method.

179

180 **Table 2.** TD-GC/MS method validation parameters for the 16 EPA PAHs in NIST SRM 1649b
 181 urban dust (n=10).

PAH	Experimental mean (ng) ^a	NIST certified value (ng) ^a	RSD (%)	Recovery (%)
Naph	3694.41 ± 1082.45	26.75 ± 2.98	46.33	13808.82
Acy	6.97 ± 0.61	1.99 ± 0.24	13.86	351.11
Ace	1.57 ± 0.19	2.03 ± 0.41	19.53	77.25
FL	2.06 ± 0.21	2.29 ± 0.67	16.40	89.88
Phe	42.70 ± 3.25	45.28 ± 0.21	12.02	94.30
Ant	12.59 ± 0.78	10.06 ± 0.22	9.82	125.12
Ft	59.57 ± 3.22	67.91 ± 0.41	8.56	87.71
Pyr	51.76 ± 2.80	51.24 ± 1.44	8.56	101.01
BaA	19.26 ± 1.06	21.71 ± 0.51	8.70	88.70
Chry	26.17 ± 1.32	31.33 ± 0.29	7.95	83.52
BbFt + BjFt	75.00 ± 6.17	81.34 ± 2.29	13.01	92.21
BkFt	16.09 ± 1.37	17.51 ± 0.50	13.43	91.85
BaP	20.38 ± 1.48	25.42 ± 2.47	11.52	80.18
IP	35.49 ± 1.94	29.74 ± 1.65	8.63	119.34
DBahA+DBacA	6.35 ± 0.93	6.02 ± 0.11	23.11	105.42
BghiP	37.21 ± 2.19	40.85 ± 0.41	9.31	91.10
Average^b	-	-	12.18	96.67

182 ^a expanded uncertainty about the mean, with coverage factor, k = 2.

183 ^b except Naph and Acy.

184

185 **Table 3.** Soxhlet extraction-GC/MS method validation parameters for the 16 EPA PAHs in SRM
 186 1649b (n=7).

PAH	Experimental mean (ng) ^a	NIST certified value (ng) ^a	RSD (%)	Recovery (%)
Naph	67.32 ± 18.60	391.64 ± 35.43	33.84	17.19
Acy	20.17 ± 5.91	79.90 ± 9.48	35.86	25.24
Ace	24.99 ± 5.41	81.56 ± 16.48	26.53	30.65
FL	32.60 ± 9.18	92.32 ± 14.42	34.49	35.31
Phe	1215.35 ± 331.78	1668.42 ± 24.72	33.43	72.84
Ant	104.55 ± 25.71	169.12 ± 1.65	32.53	61.82
Ft	2392.52 ± 559.83	2573.91 ± 32.96	30.95	92.95
Pyr	1914.67 ± 398.71	2054.18 ± 57.68	27.55	93.21
BaA	808.28 ± 148.46	870.34 ± 20.60	24.30	92.87
Chry	1632.01 ± 464.16	1256.02 ± 11.54	37.62	129.94
BbFt+BjFt	3144.07 ± 800.72	3260.70 ± 91.88	33.69	96.42
BkFt	921.46 ± 319.73	702.05 ± 20.19	45.90	131.25
BaP	1019.58 ± 271.00	1018.84 ± 98.88	35.16	100.07
IP	1109.96 ± 296.97	1192.08 ± 65.92	35.39	93.11
DBahA+DBacA	507.81 ± 176.18	241.30 ± 4.53	45.90	363.16
BghiP	2143.65 ± 580.24	1777.81 ± 32.96	35.81	120.58
Average^b	-	-	34.85	120.69

^a expanded uncertainty about the mean, with coverage factor, $k = 2$.

^b except Naph, Acy, Ace and FL.

187
188
189

190 Although the chromatographic column used in this study demonstrated a good resolution for the
191 16 EPA PAHs, the presence of other PAHs in the standard reference material can generate co-
192 elution problems (Bordajandi *et al.*, 2008). Thus, in the results obtained from the analysis of
193 SRM 1649b, the BbFt and DBahA presented co-elution with the benzo[j]fluoranthene (BjFt) and
194 dibenzo[a,c]anthracene (DBacA), respectively.

195 The most compounds for both methods accomplished the quality objectives for ambient air PAHs
196 stated by ISO 12884:2000, which establishes recovery efficiency between 75 and 125 %, and a
197 precision of ± 25 %. However, the lowest molecular weight PAHs (Naph and Acy) were
198 overestimated (recoveries > 125 %) when they were analyzed by the TD-GC/MS method. These
199 compounds could suffer losses during the sample preparation due their high volatility.

200 In the case of Soxhlet extraction, the lightest PAHs (Naph, Acy, Ace and FL) showed low
201 recoveries (< 75 %). The loss of these analytes during the extraction process in the Soxhlet Warm
202 mode could be the main reason for these low recoveries. On the other hand, the DBahA
203 concentration (pair DBahA-DBacA) was overestimated (recovery of 210 %).

204 Hence, the PAHs that did not accomplished the quality objective stated by ISO 12884:2000 were
205 excluded from the study.

206

207 *Uncertainty estimation*

208 The particle-bound PAH concentrations in the air samples, expressed in ng m^{-3} , are obtained from
209 the following equations, Eq. (1) for TD-GC/MS and Eq. (2) for Soxhlet-GC/MS:

210

$$211 \quad \text{Concentration} (\text{ng} \cdot \text{m}^{-3}) = \frac{C (\text{ng} \cdot \text{mL}^{-1}) \cdot A_s (\text{m}^2)}{V_{\text{air}} (\text{m}^3)} \quad (1)$$

212

$$213 \quad \text{Concentration} (\text{ng} \cdot \text{m}^{-3}) = \frac{C (\text{ng} \cdot \text{mL}^{-1}) \cdot V_s (\text{mL})}{V_{\text{air}} (\text{m}^3)} \quad (2)$$

214

215 where C is the concentration of the target compound obtained from the calibration (ng m^{-2} or ng
216 mL^{-1}); A_{sample} is the final area of the analyzed filter (m^2); V_{sample} is the final volume of the sample
217 (mL); V_{air} is the volume of the air sampled (m^3).

218 According to Eq. (1) and (2), the main uncertainty sources that contributed to the determination
219 of particle PAHs in air are:

220 - Analytical determination (calibration).

221 - Extraction stage (recovery).

222 - Applicability in ambient air samples (A_s or V_s and V_{air}).

223 The uncertainty associated with the method (u_{comb}) was calculated by combining the uncertainty
224 derived from each source (Eq. 3).

225

$$226 \left(\frac{u_{comb}}{C} \right)^2 = \left(\frac{u(Cal)}{C} \right)^2 + \left(\frac{u(R)}{R} \right)^2 + \left(\frac{u(A_s \text{ or } V_s)}{A_s \text{ or } V_s} \right)^2 + \left(\frac{u(V_{air})}{V_{air}} \right)^2 \quad (3)$$

227

228 where $u(Cal)$ is the calibration uncertainty (ng); $u(R)$ is the uncertainty derived from recovery;
229 $u(A_s \text{ or } V_s)$ is the uncertainty derived from area (m^2) or volume (μL) of sample; $u(V_{air})$ is the
230 uncertainty derived from air volume; C is the amount of analyte (ng); R is the recovery; A_s is the
231 area of the filter (m^2); V_s is the volume of sample injected (μL) and V_{air} is the volume of air
232 sampled (m^3).

233

234 *Uncertainty derived from the analytical determination.*

235 The uncertainty associated with calibration, $u(Cal)$, was determined by taking the square root of
236 the sum of the squares of the uncertainty derived from calibration curve adjustment and solutions
237 preparation (standard and internal standard solutions) (Eq. 4).

238

$$239 \left(\frac{u(Cal)}{C} \right)^2 = \left(\frac{u(C_x)}{C_x} \right)^2 + \sum_{i=1}^n \left(\frac{u(std)}{C_{std}} \right)^2 + \sum_{j=1}^m \left(\frac{u(is)}{C_{is}} \right)^2 \quad (4)$$

240

241 where $u(C_x)$ is the uncertainty derived from linear least squares adjustment; $u(std)$ is the
242 uncertainty derived from standard solution preparation; $u(is)$ is the uncertainty derived from
243 internal standard solution preparation; C_x is the predicted analyte concentration; C_{std} is the
244 standard solution concentration; C_{is} is the internal standard solution concentration; n is the level

245 of target compounds in the calibration curve; and m is the level of deuterated compounds in the
246 calibration curve.

247

248 *Uncertainty derived from linear least squares adjustment, $u(C_x)$.*

249 The uncertainty derived from the linear least squares adjustment is mainly due to the variability
250 in the responses shown by the instrument, and it is evaluated from standard deviations of slope
251 and intercept in calibration line. The relative uncertainty of the predicted analyte concentration
252 ($u(C_x)/C_x$) from linear least squares adjustment was calculated applying the following
253 equation (Barrado-Olmedo *et al.* 2012):

254

$$255 \left(\frac{u(C_x)}{C_x} \right)^2 = \frac{u_y^2}{(y-b)^2} + \frac{u_b^2}{(y-b)^2} + \frac{u_m^2}{(m)^2} \quad (5)$$

256

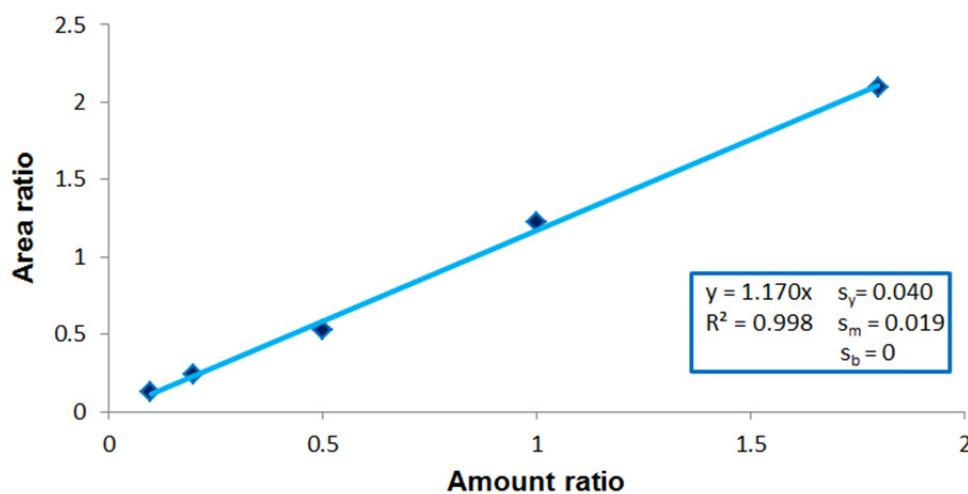
257 where y is the mean value of the analytical response of the calibration curve; u_y is the uncertainty
258 of the response deduced from its standard deviation (s_y) for n calibration points (s_y/\sqrt{n}); b is the
259 y-intercept of the calibration curve; u_b is the uncertainty of y-intercept deduced from its standard
260 deviation (s_b) for n calibration points (s_b/\sqrt{n}); m is the slope; and u_m is the uncertainty of
261 slope deduced from its standard deviation (s_m) for n calibration points (s_m/\sqrt{n}).

262 In both methods (TD-GC/MS and Soxhlet-GC/MS), internal calibration curves of five
263 concentration levels were used to calibrate. Internal calibration curves were plotted as the ratio of
264 peak area (analyte/deuterated) versus the ratio of amount in ng (analyte/deuterated). In TD-
265 GC/MS, different amounts of PAHs (from 2.5 ng to 45 ng) and the same amount of deuterated
266 compounds (25 ng) were spiked in a portion of filter introduced into sampling tube. In the case of

267 Soxhlet-GC/MS, PAH levels between 0.2 and 5 ng and deuterated PAHs of 1 ng were used to
268 calibrate.

269 For example, an internal calibration curve of BaP by TD-GC/MS was performed (Fig. 1),
270 showing a slope value of 1.170 and a correlation coefficient of 0.998. The mean value of the area
271 ratio (the analytical response of curve) was 0.841.

272



273

274

Fig. 1. Calibration curve of BaP in TD-GC/MS.

275

276 Finally, the relative $(u(C_x)/C_x)$ for BaP was determined by Eq. 6.

277

$$\frac{u(C_x)}{C_x} = \sqrt{\frac{(0.040/\sqrt{5})^2}{(0.841)^2} + \frac{(0.019/\sqrt{5})^2}{(1.170)^2}} = 0.02 \quad (6)$$

279

280 Table 4 shows the relative uncertainty associated with the calibration curve for each PAH in both
281 methods (TD-GC/MS and Soxhlet-GC/MS). The results ranged between 0.02 and 0.06 for TD-
282 GC/MS, and between 0.01 and 0.04 for Soxhlet-GC/MS.

283

284 **Table 4.** Relative uncertainty from linear least squares adjustment for each PAH in TD-GC/MS
 285 and Soxhlet-GC/MS method.

PAH	$(u(C_x)/C_x)$	
	TD-GC/MS	Soxhlet-GC/MS
Ace	0.04	-
FL	0.06	-
Phe	0.02	0.03
Ant	0.03	0.01
Ft	0.03	0.02
Pyr	0.03	0.03
BaA	0.02	0.03
Chry	0.04	0.02
BbFt	0.03	0.01
BkFt	0.04	0.02
BaP	0.02	0.04
IP	0.05	0.02
DBahA	0.05	0.03
BghiP	0.03	0.02

286

287 *Uncertainty derived from standard solution preparation, $u(std)$.*

288 Uncertainty associated with the preparation of calibration standards includes the uncertainty of
 289 the stock solution according to certificates and dilution chain. This uncertainty is a combination
 290 of the uncertainty of the glassware used and stock solutions. In this study, the standards were
 291 prepared using syringes (syr) and volumetric flask (flask). Eq. 7 and 8 were used to determine
 292 $u(std)$ (Aslan-Sungur *et al.* 2014).

293

$$294 \left(\frac{u(std)}{C_{std}} \right)^2 = \left(\frac{u(stock)}{C_{stock}} \right)^2 + \left(\frac{u(f)}{f} \right)^2 \quad (7)$$

295

296

$$u(f) = \sqrt{\left(\frac{u(syr)}{V_{syr}}\right)^2 + \left(\frac{u(flask)}{V_{flask}}\right)^2} \quad (8)$$

297

298 where $u(f)$ is the uncertainty of the dilution factor; $u(syr)$ is the uncertainty of the syringe; $u(stock)$
 299 is the uncertainty of the stock solution; $u(flask)$ is the uncertainty of the volumetric flask; f is the
 300 dilution factor; C_{stock} is the amount of analyte in the stock solution; V_{syr} is the volume of the
 301 syringe and V_{flask} is the volume of the flask.

302 The $u(syr)$ and $u(flask)$ were calculated as the combination of the uncertainty coming from the
 303 calibration of the tool ($u(syr_{cal})$ or $u(flask_{cal})$), and the uncertainty source from the temperature
 304 ($u(T)$) (Eq. 9 and 10).

305

$$u(syr) = \sqrt{(u(syr_{cal}))^2 + (u(T))^2} \quad (9)$$

307

$$u(flask) = \sqrt{(u(flask_{cal}))^2 + (u(T))^2} \quad (10)$$

309

310 The uncertainties from the calibration of the item ($u(syr_{cal})$ and $u(flask_{cal})$) were calculated by
 311 using manufacturer's data (Table 5), assuming a rectangular distribution.

312

313 According to the Eurachem/Citac (2012) guide, the temperature effect is the result of the
 314 variation in temperature in the laboratory which is generally accepted as ± 3 °C and can be
 315 calculated by the next equation (Yenisoy-Karakaş 2012):

316

$$u(T) = \frac{3 \cdot V \cdot Q}{1.73} \quad (11)$$

317

318

319 where $u(T)$ is the standard uncertainty of the temperature; V measured volume and Q is the
320 coefficient of volume expansion of the solvent used in the preparation.

321 Table 5 introduces the manufacturer's specification data of items used to prepare the standard
322 solution.

323

324 **Table 5.** The manufacturer's specification data of lab tools, PAH standard and solvents

Item	Amount	Manufacturer's specification
Volumetric flask	1mL	$\pm 2.50 \times 10^{-2} \text{ mL}^a$
Syringe	2; 25; 50; 125; 250; 500 μL	$\pm 1 \%$ nominal volume ^a
Standard 16 EPA-PAHs	2000 $\text{ng } \mu\text{L}^{-1}$	$\pm 11.63 \text{ ng } \mu\text{L}^{-1}$ ^b
Internal deuterated PAHs	200 $\text{ng } \mu\text{L}^{-1}$	$\pm 4 \text{ ng } \mu\text{L}^{-1}$ ^a
Methanol thermal expansion (at 25°C)	-	$1.15 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$
Methylene chloride thermal expansion (at 25°C)	-	$1.44 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$
Toluene thermal expansion (at 25°C)	-	$1.11 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$
n-Hexane thermal expansion (at 25°C)	-	$1.14 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$

325 ^a accuracy.

326 ^b expanded uncertainty (95%).

327

328 In this study, the stock solution for the TD-GC/MS method was the standard certificated mixture
329 of 16 EPA PAHs (SV Calibration Mix 5, Restek, 2000 $\mu\text{g mL}^{-1}$). To prepare the calibration
330 standards (solutions of 2.5, 5, 12.5, 25, and 45 $\text{ng } \mu\text{L}^{-1}$), two dilution stages were necessary. In
331 the first, 50 μL were removed from the stock solution and diluted in 1mL of methanol, obtaining
332 a 100 $\text{ng } \mu\text{L}^{-1}$ solution. Subsequently, and depending on the target concentration of calibration
333 solution, different volumes were removed from it and diluted with 1 mL of methanol (e.g. to
334 obtain a concentration of 2.5 $\text{ng } \mu\text{L}^{-1}$; 25 μL of a 100 $\text{ng } \mu\text{L}^{-1}$ solution were necessary). These two

335 dilution stages should be considered in the expression of uncertainty in the dilution, where the
 336 suffixes 1 and 2 mark the dilution stage (Eq.12).

337

$$338 \quad u(f) = \sqrt{\left(\frac{u(syr)_1}{V_{syr_1}}\right)^2 + \left(\frac{u(flask)_1}{V_{flask_1}}\right)^2 + \left(\frac{u(syr)_2}{V_{syr_2}}\right)^2 + \left(\frac{u(flask)_2}{V_{flask_2}}\right)^2} \quad (12)$$

339

340 Tables 6 and 7 summarize the uncertainties obtained for each dilution stage and the calibration
 341 solution in the preparation of standard solutions.

342

343 **Table 6.** Uncertainty associated with syringe and volumetric flask during the standard solution
 344 preparation for each dilution stage (TD-GC/MS method).

Dilution stage	Solution concentration (ng μL^{-1})	V_{syr} (μL)	$u(syr_{cal})$ (μL)	$u(T)$ (μL)	$u(syr)$ (μL)
1 st	100	50	0.29	0.13	0.31
2 nd	2.5	25	0.14	0.05	0.15
2 nd	5	50	0.29	0.10	0.31
2 nd	12.5	125	0.72	0.25	0.76
2 nd	25	250	1.44	0.50	1.53
2 nd	45	450	2.60	0.90	2.75

Dilution stage	Solution concentration (ng μL^{-1})	V_{flask} (μL)	$u(flask_{cal})$ (μL)	$u(T)$ (μL)	$u(flask)$ (μL)
1 st ; 2 nd	100; 2.5; 5; 12.5; 25; 45	1000	14.43	2	14.57

345

346 **Table 7.** Relative uncertainties associated with dilution and standard solution preparation for
 347 each calibration solution (TD-GC/MS method).

Solution concentration (ng μL^{-1})	f	$u(f)$	C stock (ng μL^{-1})	$u(stock)$ (ng μL^{-1})	$u(std)/C_{std}$
2.5	800	0.02	2000	5.82	$2.91 \cdot 10^{-3}$
5	400	0.02	2000	5.82	$2.91 \cdot 10^{-3}$
12.5	160	0.02	2000	5.82	$2.91 \cdot 10^{-3}$

25	80	0.02	2000	5.82	$2.92 \cdot 10^{-3}$
45	44	0.02	2000	5.82	$2.95 \cdot 10^{-3}$

348

349 The relative uncertainty associated with standard solution preparation ($u(\text{std})/C_{\text{std}}$) presented
 350 very similar values for the different calibration solutions (ranging between $2.91 \cdot 10^{-3}$ and
 351 $2.95 \cdot 10^{-3}$). The contribution of temperature in the uncertainty of syringe and volumetric flask
 352 was negligible, being the uncertainty of the stock solution the major uncertainty contributor to the
 353 uncertainty in the preparation of the standard solution.

354 The same calculations were performed for the Soxhlet-GC/MS. In this method, the calibration
 355 standards (solutions of 0.1, 0.25, 0.5, 1 and 2.5 $\text{ng } \mu\text{L}^{-1}$) were prepared in three dilution stages:

- 356 - 50 μL were removed from the stock solution (SV Calibration Mix 5, Restek, 2000 $\mu\text{g mL}^{-1}$
 357 1) and diluted in 1 mL of methanol, obtaining a 100 $\text{ng } \mu\text{L}^{-1}$ solution.
- 358 - 100 μL of 100 $\text{ng } \mu\text{L}^{-1}$ solution were diluted in 1 mL of methanol (10 $\text{ng } \mu\text{L}^{-1}$ solution).
- 359 - Finally, from 10 $\text{ng } \mu\text{L}^{-1}$ solution, different volumes were removed and diluted to obtain
 360 the calibration solutions.

361 Table 8 shows the results obtained in the determination of the uncertainties associated with lab
 362 tools for the Soxhlet-GC/MS method.

363

364 **Table 8.** Uncertainties associated with syringe and volumetric flask during the standard solution
 365 preparation for each dilution stage (Soxhlet -GC/MS method).

Dilution stage	Solution concentration ($\text{ng } \mu\text{L}^{-1}$)	V_{syr} (μL)	$u(\text{syr}_{\text{cal}})$ (μL)	$u(\text{T})$ (μL)	$u(\text{syr})$ (μL)
1 st	100	50	0.29	0.13	0.31
2 nd	10	100	0.58	0.20	0.61
3 rd	0.1	10	0.06	0.02	0.06
3 rd	0.25	25	0.14	0.05	0.15
3 rd	0.5	50	0.29	0.10	0.31

3 rd	1	100	0.58	0.20	0.61
3 rd	2.5	250	1.44	0.50	1.53
Dilution stage	Solution concentration (ng μL^{-1})	V_{flask} (μL)	$u(\text{flask}_{\text{cal}})$ (μL)	$u(T)$ (μL)	$u(\text{flask})$ (μL)
1 st ; 2 nd ; 3 rd	100; 10; 2.5; 5; 12.5; 25; 45	1000	14.43	2	14.57

366

367 The results of Table 8 were used in Eq.12 and 7, obtaining the same relative uncertainty in the
368 preparation of the different calibration solutions, $2.91 \cdot 10^{-3}$. This value was the same as that
369 obtained for the preparation of solutions of 2.5, 5 and 12.5 ng μL^{-1} in the TD-GC/MS method.
370 Again, the uncertainty of the stock solution was the main contributor to the uncertainty in the
371 preparation of the standard solution, whereas, the effect of the temperature was negligible in the
372 uncertainty associated with lab tools.

373

374 *Uncertainty derived from internal standard solution preparation, $u(is)$.*

375 To determine the uncertainty associated with internal standard solution preparation the same
376 methodology was used in the assessment of $u(\text{std})$.

377 In the TD-GC/MS, a solution of 25 ng μL^{-1} was prepared from stock solution (Predeuterated
378 internal standard PAH Mixture 6 Chiron, 200 $\mu\text{g mL}^{-1}$), removing 125 μL and diluting them in 1
379 mL of methanol. For the Soxhlet-GC/MS, the internal solution added to samples was the result of
380 two dilution stages: 100 μL of stock solution (the same as in the TD-GC/MS method) was
381 removed and diluted in 1 mL of methanol, obtaining a 20 ng μL^{-1} ; subsequently, 25 μL from this
382 solution were diluted in 1 mL of methanol to get a final concentration of 0.5 ng μL^{-1} .

383 The relative uncertainty $u(is)/C_{is}$ obtained for the TD-GC/MS and Soxhlet-GC/MS methods
384 were 0.02 and 0.01 respectively. In the case of the TD-GC/MS, due to the dilution factor was low
385 ($f = 8$), both terms of Eq. 7 (stock solution and dilution factor) had a similar contribution to the

386 uncertainty in the preparation of the internal standard solution. In contrast, for the Soxhlet-
 387 GC/MS method, the effect of the dilution factor was negligible, being the uncertainty of the stock
 388 solution the main contributor.

389

390 *Uncertainty derived from calibration, $u(Cal)$.*

391 Once $(u(C_x)/C_x)^2$, $(u(std)/C_{std})^2$ and $(u(is)/C_{is})^2$ had been calculated, the relative
 392 uncertainty derived from the calibration was estimated according to Eq.4. For BaP (determined
 393 by the TD-GC/MS method) the calculation was as follows:

394

$$395 \left(\frac{u(Cal)}{C}\right)^2 = (0.02)^2 + (2.91 \cdot 10^{-3})^2 + (2.91 \cdot 10^{-3})^2 + (2.91 \cdot 10^{-3})^2 + \quad (13)$$

$$(2.92 \cdot 10^{-3})^2 + (2.95 \cdot 10^{-3})^2 + (0.02)^2 = 8.43 \cdot 10^{-4}$$

396

$$397 \frac{u(Cal)}{C} = \left(\sqrt{8.43 \cdot 10^{-4}}\right) = 0.03 \quad (14)$$

398

399 The relative uncertainty $u(Cal)/C$ associated with the calibration for each PAH in the TD-GC/MS
 400 and Soxhlet-GC/MS methods are summarized in Table 9.

401

402 **Table 9.** Relative uncertainty for each PAH in the TD-GC/MS and Soxhlet-GC/MS methods.

PAH	$(u(Cal)/C)$	
	TD-GC/MS	Soxhlet-GC/MS
Ace	0.04	-
FL	0.06	-
Phe	0.03	0.04
Ant	0.04	0.02
Ft	0.04	0.02
Pyr	0.04	0.03

BaA	0.03	0.03
Chry	0.05	0.02
BbFt	0.04	0.01
BkFt	0.05	0.02
BaP	0.03	0.04
IP	0.05	0.02
DBahA	0.06	0.04
BghiP	0.03	0.02

403

404 The relative uncertainty associated with calibration in both methods showed slightly lower values
 405 for Soxhlet-GC/MS (between 0.01 and 0.04 for most PAHs), since the calibration in this method
 406 was carried out by direct injection into the GC/MS. In both methods, the uncertainty derived
 407 from standard solution preparation was negligible, being the linear least squares adjustment and
 408 the internal standard solution preparation the main contributors to the uncertainty of the
 409 calibration.

410

411 *Uncertainty derived from recovery, $u(R)$.*

412 The recovery of PAHs (R) and its uncertainty ($u(R)$) were determinate from replicate
 413 measurements of standard reference material (SRM 1649b urban dust). R was considered as the
 414 ratio (C_{obs}/C_{SRM}) of the observed amount of analyte C_{obs} (mean of replicate analysis) to a
 415 reference value C_{SRM} . The relative uncertainty for recovery was calculated by using the following
 416 equations (Barwick and Ellison, 1999):

417

$$418 \left(\frac{u(R)}{R} \right)^2 = \left(\frac{u(C_{obs})}{C_{obs}} \right)^2 + \left(\frac{u(C_{SRM})}{C_{SRM}} \right)^2 \quad (15)$$

419

420
$$\frac{u(C_{obs})}{C_{obs}} = \frac{SD}{C_{obs} \cdot \sqrt{n}} \quad (16)$$

421

422 where $u(C_{obs})/C_{obs}$ is the relative uncertainty derived from the observed amount of analyte after
 423 the extraction; $u(C_{SRM})/C_{SRM}$ is the relative uncertainty derived from the amount of analyte in
 424 the SRM; SD is the standard deviation of the results from the replicate analyses of the SRM and n
 425 is the number of replicates.

426 For BaP, determined by the TD-GC/MS method:

427

428
$$\frac{u(R)}{R} = \sqrt{\left(\frac{0.74 \text{ ng}}{20.38 \text{ ng}}\right)^2 + \left(\frac{1.24 \text{ ng}}{25.42 \text{ ng}}\right)^2} = 0.06 \quad (17)$$

429

430 The R and $(u(R)/R)$ values for each PAH were determined for both methods (Table 10) from
 431 results obtained during the method validations (Table 2 and 3).

432

433 **Table 10.** Relative recovery uncertainties of PAH obtained from the analysis of NIST SRM
 434 1649b (n=10) by TD-GC/MS and Soxhlet-GC/MS (n=7).

PAH	u(R)/C	
	TD-GC/MS	Soxhlet-GC/MS
Ace	0.12	-
FL	0.15	-
Phe	0.03	0.14
Ant	0.03	0.12
Ft	0.03	0.12
Pyr	0.03	0.11
BaA	0.03	0.09
Chry	0.03	0.14

BbFt	0.04	0.13
BkFt	0.04	0.17
BaP	0.06	0.14
IP	0.04	0.14
DBahA	0.07	-
BghiP	0.03	0.14

435

436 Regarding relative recovery uncertainty, for TD-GC/MS method, it ranged from 0.03 to 0.15 for
 437 target PAHs. Among the compounds, only Ace and FL showed the highest values (> 0.07). Their
 438 low concentrations in particulate phase and their high volatility could explain this increase in the
 439 relative recovery uncertainty.

440 In contrast, Soxhlet-GC/MS method showed higher relative recovery uncertainty (values between
 441 0.09 and 0.17).

442

443 *Uncertainty derived from the applicability in ambient air samples, $u(A_s)$ or $u(V_s)$ and*
 444 *$u(V_{air})$*

445 In the TD-GC/MS the possible size variations in the cutting of the filter could be a source of
 446 uncertainty. Grandesso *et al.* (2013), analyzing particle PAHs by TD-GC/MS method, estimated
 447 a relative uncertainty derived from cutting (u_{cut}/C) of $7.60 \cdot 10^{-3}$. Thus, this value was
 448 considered in this study for the TD-GC/MS method. The term of $u(A_s)/A_s$ in the combined
 449 uncertainty expression (Eq. 3) was replaced by u_{cut}/C for the TD- GC/MS method.

450 In the Soxhlet-GC/MS method the sample is injected directly into the CG/MS system, thus, the
 451 uncertainty associated with the sample in this case was the uncertainty of the syringe. The
 452 injected volume was 2 μL and relative($u(V_s)/V_s$) was calculated by the Eq. 12, obtaining a
 453 value of 0.01 for each PAH.

454 $(u(V_{\text{air}})/V_{\text{air}})$ is related to the uncertainty of the air sampler. In both methods (TD-GC/MS and
 455 Soxhlet-GC/MS), the air sampler (Digital DHA-80) worked at $30 \text{ m}^3 \text{ h}^{-1}$ during 8 h (total volume
 456 of air collected per sample of 240 m^3). The relative uncertainty of this sampler in the flow (u_{sampler})
 457 was estimated by the manufacturer in $\pm 1.03 \%$, thus, the relative uncertainty derived from the
 458 air volume for both methods is as follows:

$$\frac{u(V_{\text{air}})}{V_{\text{air}}} = \frac{2.47 \text{ m}^3}{240 \text{ m}^3} = 0.01 \quad (18)$$

462 *Combined uncertainty, u_{comb} .*

463 Finally, the relative combined uncertainty for 16 EPA PAHs in each method was calculated by
 464 Eq. 3. BaP (determined by the TD-GC/MS method) is given as an example calculation in Eq. 19.

$$\frac{u_{\text{comb}}}{C} = \sqrt{(0.03)^2 + (0.06)^2 + (7.60 \cdot 10^{-3})^2 + (0.01)^2} = 0.07 \quad (19)$$

468 Table 11 shows the relative combined uncertainty in % for each PAH in both methods.

470 **Table 11.** u_{comb}/C and for 16 EPA PAHs in both methods.

PAH	u_{comb}/C (%)	
	TD-GC/MS	Soxhlet-GC/MS
Ace	13	-
FL	17	-
Phe	5	14
Ant	5	13
Ft	5	12
Pyr	5	11

BaA	4	10
Chry	6	15
BbFt	6	13
BkFt	7	18
BaP	7	15
IP	7	14
DBahA	9	-
BghiP	5	14

471

472 According to the results, the TD-GC/MS method was more reliable than Soxhlet-GC/MS for the
 473 determination of particulate PAHs, with lower combined uncertainties (< 8 % for most PAHs),
 474 since the Soxhlet extraction requires a slower and laborious sample preparation stage, which
 475 increases the measurement uncertainty.

476 In terms of the contribution, for TD-GC/MS the recovery uncertainty had similar values than
 477 calibration uncertainty. Therefore, the highest impacts on measurement uncertainty for this
 478 method arise from calibration and recovery, except in the determination of the lowest molecular
 479 weight PAHs (Ace and FL), where the recovery was the main uncertainty contributor. In the case
 480 of Soxhlet-GC/MS, the highest uncertainty source came from recovery of extraction stage.

481

482 CONCLUSIONS

483

484

485 Two analytical methods based on different extraction technique (TD-GC/MS and Soxhlet-
 486 GC/MS) were applied to analyze particle-bound PAHs in air samples. Both methods were
 487 validate by standard reference material (urban dust), demonstrating that TD-GC/MS is a more
 488 reliable method to determinate these compounds in aerosol samples, with an average recovery
 489 efficiency of 96.67 and mean RSD values of 12.18.

490 Uncertainties associated with the determination of particle-bound polycyclic aromatic
491 hydrocarbons (PAHs) in air samples by TD-GC/MS and Soxhlet-GC/MS method were estimated.
492 Calibration curve, recovery, area or volume of sample and volume of air were identified as main
493 uncertainty sources for both methods. The combined uncertainty associated with TD-GC/MS
494 method was about 5-9 % for most PAHs, being the calibration curve and recovery the main
495 contributors.

496 The extraction of PAHs by a solvent extraction-based method (Soxhlet extraction) showed higher
497 uncertainty (percentages between 11-18 % for most compounds), mainly due to the uncertainty
498 from recovery. The high manipulation of the sample during Soxhlet extraction could explain
499 these values.

500

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502

503

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508

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