

1 **Joint quantification of PAH and oxy-PAH from standard reference**
2 **materials (urban dust and diesel particulate matter) and diesel soot**
3 **surrogate by GC-MS**

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10

11 **Abstract**

12 The combustion of fossil fuels produces pollutants such as soot, which consists of carbonaceous
13 particles whose emission is regulated by environmental laws. Soot is mainly formed from
14 polycyclic aromatic hydrocarbons (PAH), through different reaction ways and, once formed, it
15 can adsorb PAH on its surface. These compounds have an environmental importance due to
16 their carcinogenic and mutagenic potential. In the last years, the oxygenated derivatives of PAH
17 (oxy-PAH) have also been considered as dangerous since they have been found to be mutagenic
18 for bacterial and human cells. Therefore, the purpose of this work was to quantify
19 simultaneously selected PAH and oxy-PAH from different samples of soot. The quantification
20 method involves Soxhlet extraction and subsequent concentration by rotary evaporation that
21 allows to recover the analysed compounds from soot samples. The PAH and oxy-PAH were
22 identified and quantified, by a single injection, using a gas chromatograph-mass spectrometer
23 (GC-MS). The method showed a good repeatability using a diesel soot surrogate test sample,
24 Printex-U. The validation process showed that most of the compounds are recovered between
25 the values established for the Standard Reference Materials analysed, 1650b and 1649b. The
26 values of the mass fraction of the oxy-PAH obtained in this work showed, in general, a good
27 match with those indicated in other studies.

28

29 **Keywords:** Polycyclic aromatic hydrocarbons (PAH), oxygenated polycyclic aromatic
30 hydrocarbons (oxy-PAH), gas chromatography–mass spectrometry (GC-MS), Standard
31 Reference Materials (SRM), diesel, soxhlet extraction.

32

33

34 1. Introduction

35 The atmospheric pollutant emissions are mainly produced in the combustion processes,
36 especially through the combustion of fossil fuels. Among the common pollutants, the
37 particulate matter is one of the most controlled by environmental regulations and a significant
38 fraction of it is soot, a carbonaceous material formed in the combustion process. Soot is
39 produced through the polycyclic aromatic hydrocarbons (PAH) formed in rich fuel conditions.
40 PAH formation and consecutive soot production are explained by some mechanisms such as
41 the hydrogen-abstraction/acetylene-addition (HACA) route, the combinative growth
42 mechanism, and the cyclopentadienyl recombination (Richter and Howard 2000). Oxy-PAH
43 can also be formed directly from combustion processes or in the atmosphere from PAH induced
44 oxidation (Allen et al. 1997; Albinet et al. 2008). Thus, 9-fluorenone; 9,10 anthraquinone;
45 benzanthrone and benz-[a]anthracene-7,12-dione are the most abundant oxy-PAH found in
46 ambient air (Shen et al. 2011).

47 Moreover, polycyclic aromatic hydrocarbons can be adsorbed on soot surface (Mathieu et
48 al. 2007) and could be hazardous for human health, due to their toxic character (Bosetti et al.
49 2007). The toxicity of the PAH has been repeatedly demonstrated (Durant et al. 1996), being
50 benzo[a]pyrene used in many environmental studies as a toxicity reference compound
51 (Hattemer-Frey and Travis 1991; Masiol et al. 2012; Pongpiachan et al. 2015). The US
52 Environmental Protection Agency (EPA) has established a list of 16 PAH as priority pollutants
53 (EPA-PAH) found in the atmosphere, due to their carcinogenic potential.

54 In this way, oxy-PAH have also been studied in order to determine their toxicity (Lampi et
55 al. 2005; Fu et al. 2012), in particular in human cells (Durant et al. 1996), where some ketones
56 and quinones such as benzanthrone and benzo[cd]pyrenone are denoted as mutagenic
57 compounds. Consequently, oxy-PAH have to be considered, according to Lundstedt et al.
58 (2007), for monitoring programs in contaminated sites due to their high mobility in the

59 environment. Hence, some studies involved in control of atmospheric pollution have considered
60 important to measure together oxy-PAH and PAH in urban air (Walgraeve et al. 2015; Bandowe
61 et al. 2014).

62 The quantification of PAH and oxy-PAH has been performed through different procedures.
63 A method of quantification of the 16 most important EPA-PAH, from solid and gas phases, has
64 been developed previously by our group. The method includes Soxhlet extraction,
65 concentration by rotary evaporation and subsequent gas chromatography mass spectrometry
66 (GC-MS) analysis (Sánchez et al. 2013). On the other hand, oxy-PAH have been quantified in
67 different works. Nocun and Schantz (2013) and Layschock et al. (2010) used pressurized liquid
68 extraction (PLE) and later analysis with GC-MS. O'Connell et al. (2013) quantified oxy-PAH
69 by GC-MS and liquid chromatography-atmospheric pressure chemical ionization-mass
70 spectrometry (LC-APCI-MS) and Ahmed et al. (2015) used liquid chromatography-gas
71 chromatography-mass spectrometry system (LC-GC-MS). The works mentioned above have
72 employed different Standard Reference Materials (SRM) to validate their analytical
73 methodology.

74 In this context, it has been considered interesting to develop a relatively simple method
75 through Soxhlet extraction, concentration by rotary evaporation and GC-MS analysis, that
76 allow us to quantify simultaneously selected PAH and oxy-PAH. Printex-U was used to test the
77 repeatability of the method and two Standard Reference Materials (SRM) to validate the results.

78

79 **2. Materials and methods**

80 *2.1. Reagents*

81 A PAH standard mixture (PAH-Mix 63, Dr. Ehrenstorfer-Shäfers) containing the 16 EPA-
82 PAH, and an oxy-PAH standard mixture (PAH Special Mix 7, A2S Analytical Standard
83 Solutions) containing 7 selected oxy-PAH, were employed for calibration purposes. Mix of the

84 PAH standards (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene,
85 Anthracene, Fluoranthene, Pyrene, Benzo[*a*]anthracene, Chrysene, Benzo[*b*]fluoranthene,
86 Benzo[*k*]fluoranthene, Benzo[*a*]pyrene, Indeno[1,2,3-*cd*]pyrene, Dibenz[*ah*]anthracene,
87 Benzo[*ghi*]perylene), mix of the deuterated standards of PAH (Acenaphthene d₁₀, Chrysene d₁₂,
88 Naphthalene d₈, Perylene d₁₂, Phenanthrene d₁₀) and deuterated standard of injection
89 Anthracene d₁₀ were supplied by Dr. Ehrenstorfer-Shäfers. Mix of the standards of oxy-PAH
90 (Benzo[*cd*]pyrenone, 9,10-anthraquinone, 9-fluorenone, Benzo[*a*]fluorenone,
91 Benzo[*a*]anthracene-7,12-dione, Naphthacene-5,12-dione, Benzanthrone) and mix of the
92 deuterated standards of oxy-PAH (9,10-Anthraquinone d₈, 9-Fluorenone d₈) were supplied by
93 A2S Analytical Standard Solutions.

94

95 2.2. *Experimental methodology*

96 The analytical method consists of a combination of Soxhlet extraction, concentration of the
97 extract by rotary evaporation and subsequent analysis by gas chromatography-mass
98 spectrometry. The Soxhlet extraction system was operated according to the EPA method 3540C
99 recommendations. The solvent used during the Soxhlet extraction and in the calibration was
100 dichloromethane (DCM) 99.5%. The packaging of the cellulose cartridges employed was the
101 same as used in the method developed by Sánchez et al. (2013). The temperature during the
102 extraction was 40°C and the extraction time was 24 hours with 4 cycles per hour.
103 Recommendations of EPA methods 8270D and TO-13A for determination of semivolatile
104 organic compounds and toxic organic air pollutants were taken as a reference. Internal standards
105 were used for correcting the possible losses of analytes during sample preparation, since
106 chromatographic signal of both, target compounds and their internal standards, have similar
107 responses. Calibration curves with eight concentrations levels were built. Samples of Printex-
108 U, a commercial carbon black considered as diesel soot surrogate (Arnal et al. 2012), were used

109 to test the repeatability of the method. Printex-U has been employed in different works with the
110 aim to verify the repeatability of a method (Sadezky et al. 2005; Atribak et al. 2010).

111 In order to validate the results, Standards Reference Materials, Diesel Particulate Matter
112 (1650b) (NIST 2013) and Urban Dust (1649b) (NIST 2009), were taken to verify the amount
113 of each PAH and oxy-PAH obtained in each analysis of quantification. Additionally, a
114 comparison between obtained results and those corresponding to other works was done in order
115 to check the accuracy of the present method. The PAH and oxy-PAH were jointly detected and
116 quantified by GC-MS.

117

118 *2.3. Instrumentation*

119 The extracts were analysed using GC with MS (Agilent 7890A gas chromatograph coupled
120 to an Agilent 5975C mass selective detector) operated in electron impact mode using a capillary
121 column DB-17ms (Agilent 60 m x 0.25 mm x 0.25 μm) with medium polarity, being identified
122 such as the one that provides the best results of PAH quantification, through chromatographic
123 analysis (Gómez and Wenzl 2009).

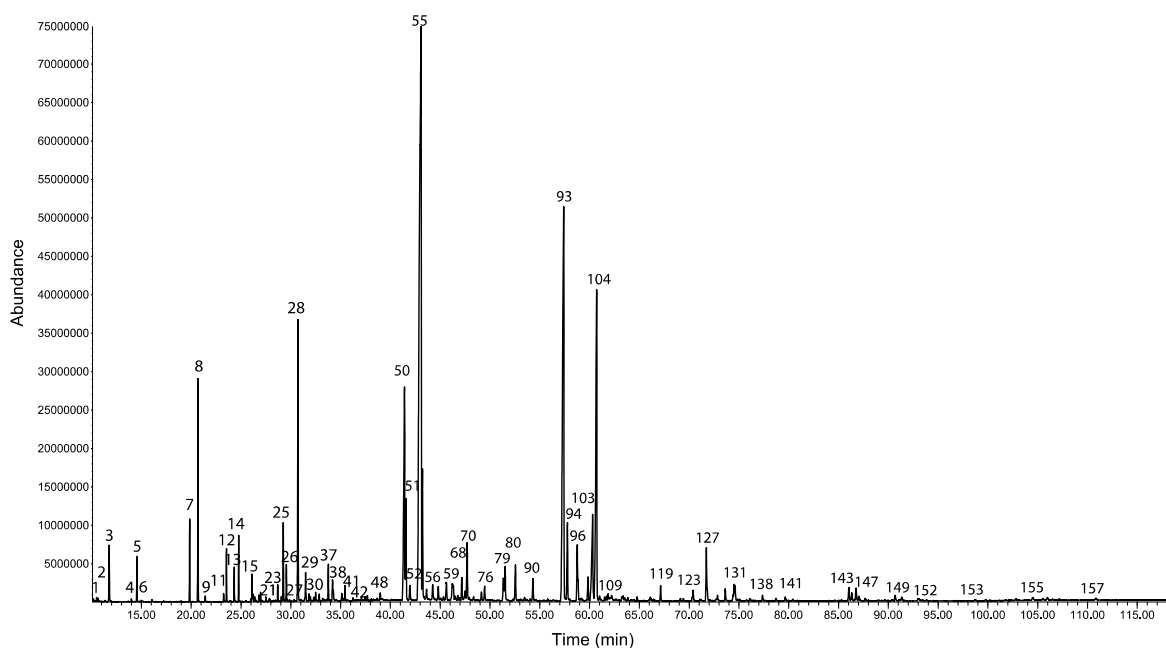
124 The chromatographic conditions always included helium as carrier gas (1 mL min^{-1}) and 2
125 μL of injection volume in splitless mode. The temperature program started at 60°C , raised 5°C
126 min^{-1} up to 190°C , then $1.5^\circ\text{C min}^{-1}$ up to 226°C , then raised $2.5^\circ\text{C min}^{-1}$ up to 288°C , finally
127 raised 1°C min^{-1} up to 320°C and held for 12 min. The transfer line temperature was 320°C .
128 The initial ion identification and determination of retention times were done using the NIST
129 spectral library, operating in SCAN mode. Once the compounds were clearly identified, the
130 analysis was performed with the selected ion monitoring (SIM), in order to increase the
131 sensitivity of the method.

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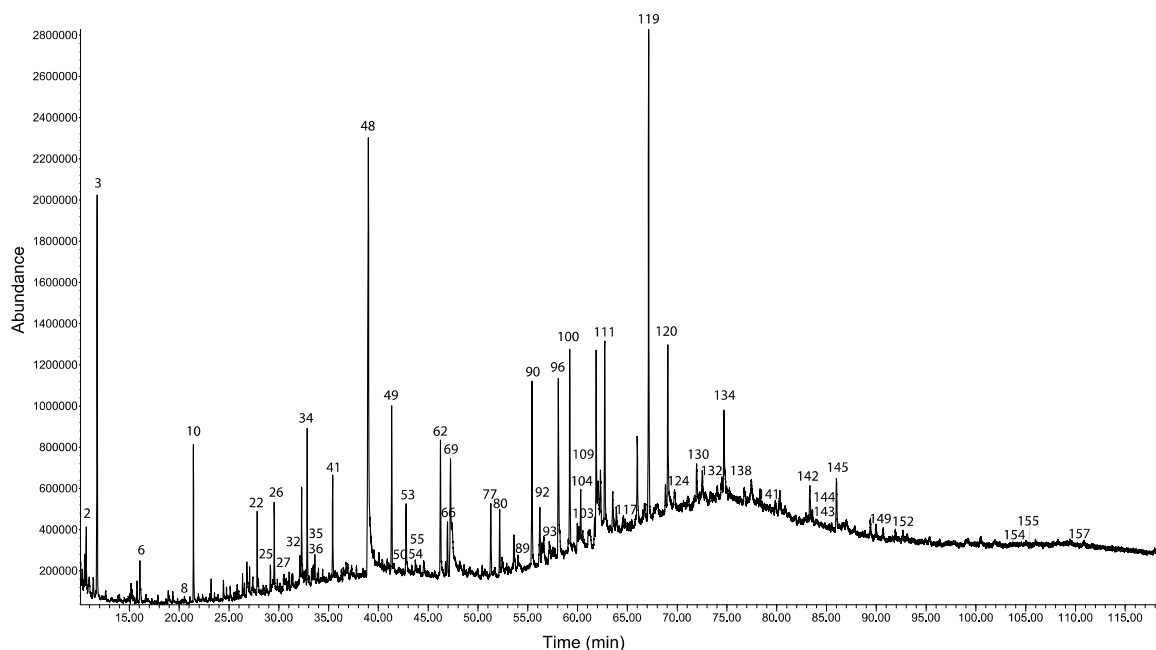
133 **3. Results and discussion**

134 3.1. Qualitative analysis by GC-MS

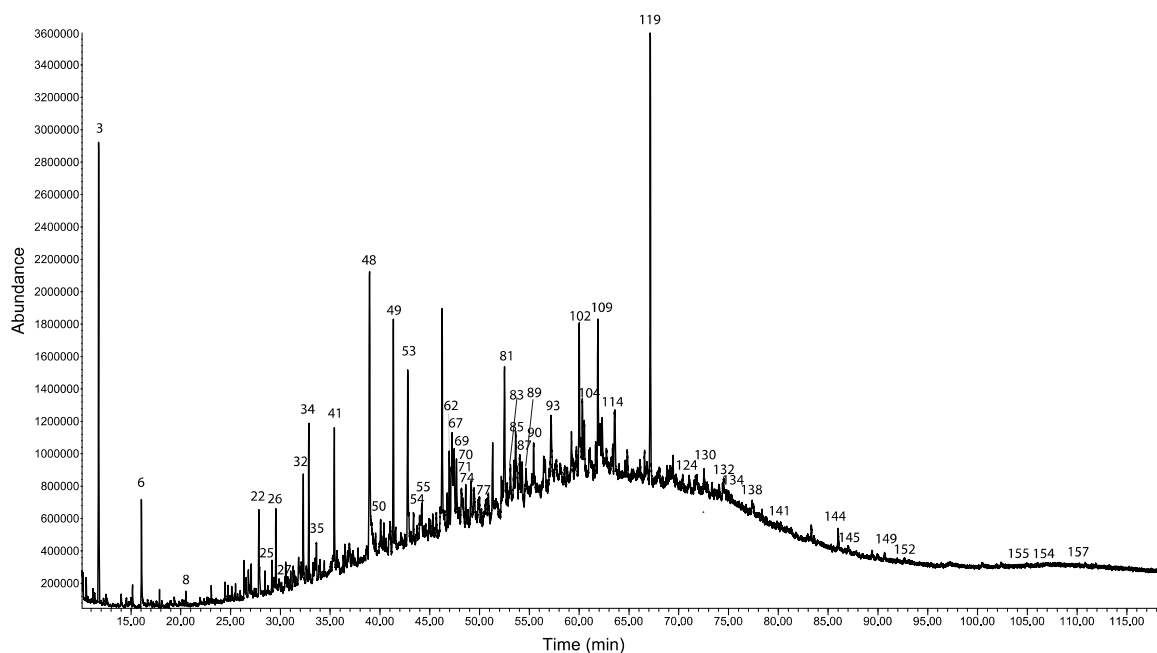
135 Qualitative analysis of extracts of different soot samples such as Printex-U and Standard
136 Reference Materials (SRM) 1649b and 1650b, was done in SCAN mode with the acquisition
137 mass range from 40 to 400 m/z, as can be seen in the chromatograms shown in the Figures 1, 2
138 and 3 respectively. 157 compounds were qualified in the three samples, and the results are
139 shown in the Table S1 of the Supplementary Material.



140
141 **Fig. 1** GC chromatogram of the Printex-U sample in SCAN mode on a DB-17MS column



142
143 **Fig. 2** GC chromatogram of the SRM 1649b sample in SCAN mode on a DB-17MS column



144
145 **Fig. 3** GC chromatogram of the SRM 1650b sample in SCAN mode on a DB-17MS column.

146 The identification of the compounds was done using the NIST spectral library. A good
147 identification was considered when match was above 70. Otherwise, the identification was only
148 considered as indicative.

149

150

151 *3.2. Quantification of PAH and oxy-PAH*

152 The linear fitting of the obtained calibration curves for each compound, indicated in section
153 2.1, showed correlation coefficients (r) between 0.988 and 0.999 within the linear range (469
154 ng mL^{-1} - 50000 ng mL^{-1}). The calibration curves were prepared in triplicate. The quantification
155 was carried out with the selected ion monitoring (SIM). The detection limit (LOD) and the
156 quantification limit (LOQ) with 95% of confidence level were also established, Table 1.

157

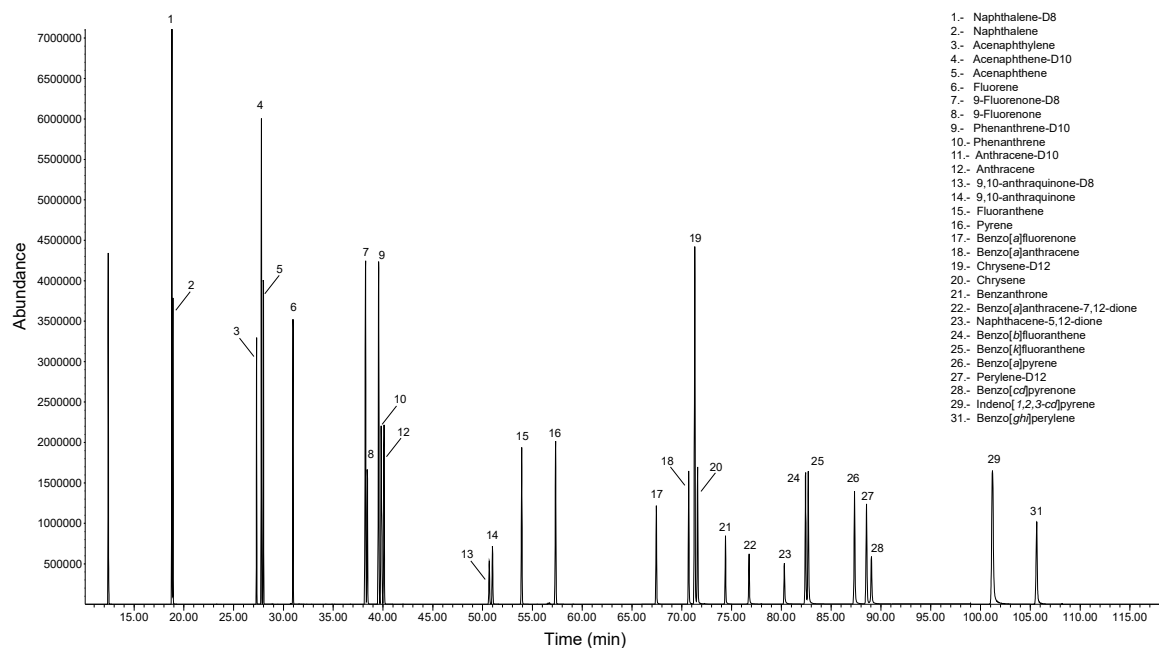
158 **Table 1.** Compounds and analytical parameters.

Compound	Molecular formula	Abbreviation	Monitored ions	RT (min)	<i>r</i>	Limit of detection LOD (ng/mL)	Limit of quantification LOQ (ng/mL)
Naphthalene ¹	C ₁₀ H ₈	NAPH	128-129	18.909	0.997	11.32	34.32
Acenaphthylene ¹	C ₁₂ H ₈	ACNY	152-153	27.308	0.997	16.82	50.98
Acenaphthene ¹	C ₁₂ H ₁₀	ACN	154-153	27.992	0.997	13.85	41.96
Fluorene ¹	C ₁₃ H ₁₀	FLUO	166-165	30.964	0.997	19.69	59.66
9-fluorenone ²	C ₁₃ H ₈ O	9-FLUO	180-152	38.433	0.997	19.59	59.36
Phenanthrene ¹	C ₁₄ H ₁₀	PHEN	178-179	39.821	0.997	16.37	49.59
Anthracene ¹	C ₁₄ H ₁₀	ANTH	178-179	40.102	0.996	24.40	73.95
9,10-anthraquinone ²	C ₁₄ H ₈ O ₂	9,10-ANTH	208-152	50.996	0.999	15.56	47.17
Fluoranthene ¹	C ₁₆ H ₁₀	FANTH	202-203	53.932	0.997	14.99	45.45
Pyrene ¹	C ₁₆ H ₁₀	PYR	202-203	57.336	0.991	16.00	48.49
Benzo[fluorenone] ²	C ₁₇ H ₁₀ O	BFLUO	230-202	67.442	0.998	23.46	71.10
Benzo[<i>a</i>]anthracene ¹	C ₁₈ H ₁₂	B[<i>a</i>]A	228-226	70.696	0.998	24.08	72.96
Chrysene ¹	C ₁₈ H ₁₂	CHR	228-226	71.594	0.997	19.40	58.79
Benzoanthrone ²	C ₁₇ H ₁₀ O	BEZO	230-202	74.396	0.996	29.85	90.46
Benzo[<i>a</i>]anthracene-7,12-dione ²	C ₁₈ H ₁₀ O ₂	7,12-BaAQ	258-202	76.765	0.999	33.05	110.16
Naphthacene-5,12-dione ²	C ₁₈ H ₁₀ O ₂	5,12-NAPQ	258-202	80.308	0.988	55.25	184.17
Benzo[<i>b</i>]fluoranthene ¹	C ₂₀ H ₁₂	B[<i>b</i>]F	252-253	82.433	0.992	28.77	87.18
Benzo[<i>k</i>]fluoranthene ¹	C ₂₀ H ₁₂	B[<i>k</i>]F	252-253	82.708	0.988	45.11	136.71
Benzo[<i>a</i>]pyrene ¹	C ₂₀ H ₁₂	B[<i>a</i>]P	252-253	87.353	0.993	26.53	80.39
Benzo[<i>cd</i>]pyrenone ²	C ₁₈ H ₁₀ O	B[<i>cd</i>]PYRO	254-226	89.047	0.994	121.94	406.46
Indeno[1,2,3- <i>cd</i>]pyrene ¹	C ₂₂ H ₁₂	I[123- <i>cd</i>]P	276-277	101.197	0.990	31.48	95.38
Dibenzo[<i>ah</i>]anthracene ¹	C ₂₂ H ₁₄	DB[<i>ah</i>]A	278-279	101.339	0.989	38.43	116.45
Benzo[<i>ghi</i>]perylene ¹	C ₂₂ H ₁₂	B[<i>ghi</i>]P	276-277	105.639	0.994	22.60	68.50

159 ¹Polycyclic aromatic hydrocarbons (PAH)160 ²Oxygenated Polycyclic aromatic hydrocarbons (oxy-PAH)

161 The chromatogram of standards and deuterated compounds used in the extraction and

162 quantification process can be seen in Figure 4.



163
 164 **Fig. 4** Chromatogram of PAH, oxy-PAH and deuterated compounds acquired in SIM mode on a DB-17MS
 165 column using GC-MS.

166

167 *3.3 Repeatability*

168 The repeatability of presented method was evaluated using Printex-U samples, considering
 169 for this purpose the results of three repetitions, using in each one 1500 mg of Printex-U.

170 Table 2 shows the average mass fraction values of the analysed PAH and oxy-PAH and
 171 their Relative Standard Deviation (RSD) values. This is a criteria acceptance for
 172 chromatographic methods, where the RSD value should be below 20% (Mahuzier et al. 2001;
 173 Choi et al. 2016). Thus, most of the obtained RSD values were lower than 27%, which can be
 174 taken as a good reference for the different quantified analytes. It can be also noticed that the
 175 higher the molecular mass was, the higher obtained. RSD value was.

176

Table 2. Average mass fraction values of PAH and oxy-PAH from Printex-U.

Compounds	Average concentration (n=3) (mg/kg)	RSD (%)
NAPH	66.48	5.99
ACNY	33.82	6.43
ACN	0.22	7.30
FLUO	1.21	11.25
9-FLUO	164.02	5.47
PHEN	857.76	6.34
ANTH	80.97	2.25
FANTH	294.77	8.65
9,10-ANTH	8.53	6.53
PYR	277.54	9.08
B[a]A	6.17	16.98
BFLUO	6.07	17.35
BEZO	3.25	25.13
CHR	10.17	17.28
7,12-BaAQ	BDL	-
5,12-NAPQ	1.19	27.02
B[cd]PYRO	11.2	14.21
B[b]F	12.85	12.38
B[k]F	6.23	17.17
B[a]P	5.06	19.36
I[123-cd]P	3.87	16.66
DB[ah]A	0.38	22.57
B[ghi]P	5.69	27.14

178 Figure 5 shows the repeatability analysis performed with Printex-U sample. It can be seen
179 that repetitions have a high precision due to low differences among them.

180 The PAH mass fraction recovered in the present study are similar to those obtained by
181 Sánchez et al. (2013), where PHEN were found in high amount and light PAH, such as NAPH
182 and ACNY, were found in low amounts.

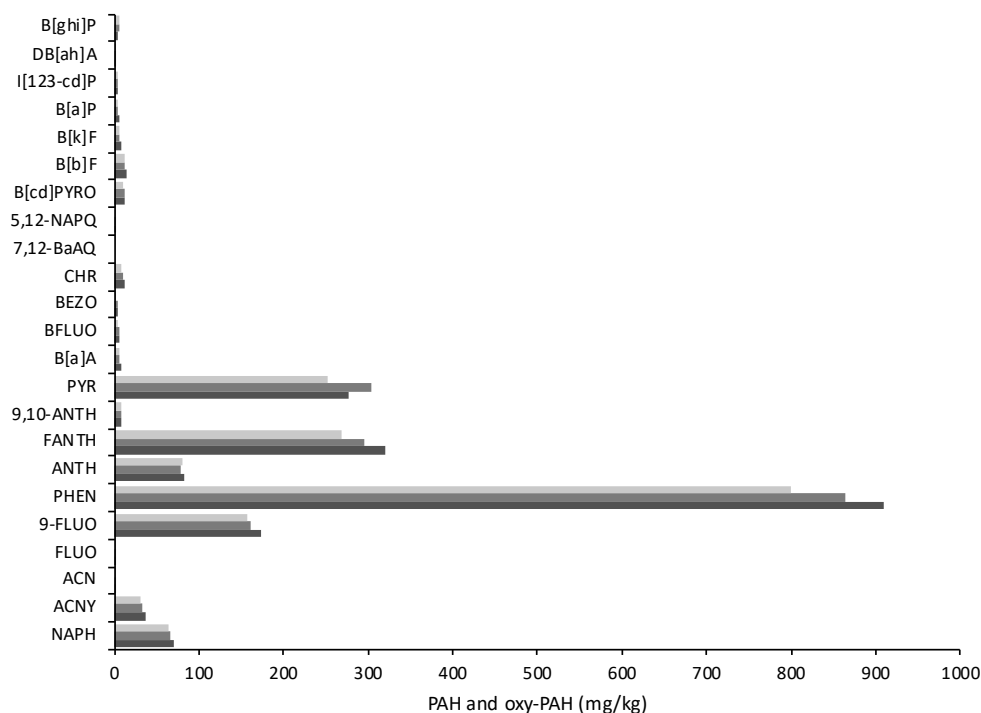


Fig 5. Repeatability obtained for Printex-U sample.

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186 3.4 Validation

187 The quantification analysis was validated using the following SRM: Diesel Particulate
 188 Matter (SRM 1650b) and Urban Dust (SRM 1649b). These SRM were commonly used in
 189 analytical works (Nocun and Schantz 2013; Layshock et al. 2010; O’Connell et al. 2013;
 190 Ahmed et al. 2015) in order to verify that the amount of the compounds obtained in each
 191 analysis corresponds to a certified value of its concentration. In this way, a high accuracy of the
 192 method is guaranteed.

193

194 **Table 3.** Average mass fraction values compared to certified/referenced concentration for SRM 1650b (standard
 195 deviations in parentheses).

Compounds	Average concentration (n=3) (mg/kg)	Certified or referenced concentration (mg/kg)
NAPH	3.69 (1.03)	5.16 ^b
ACNY	1.38 (0.68)	1.36 ^b
ACN	0.28 (0.05)	0.23 ^b
FLUO	0.95 (0.01)	0.76 ^b
9-FLUO	20.46 (1.44)	NR
PHEN	43.18 (2.01)	65.61 ^a
ANTH	5.75 (0.46)	7.58 ^b
FANTH	28.72 (2.46)	48.10 ^a
9,10-ANTH	31.39 (1.89)	NR
PYR	43.87 (7.62)	44.10 ^a
B[a]A	5.66 (1.85)	6.45 ^a
BFLUO	8.78 (1.99)	NR
BEZO	7.34 (1.14)	NR
CHR	8.53 (3.61)	13.40 ^a
7,12-BaAQ	BDL	NR
5,12-NAPQ	BDL	NR
B[cd]PYRO	28.99 (1.29)	NR
B[b]F	4.99 (1.77)	6.77 ^a
B[k]F	2.08 (1.67)	2.30 ^a
B[a]P	2.08 (0.33)	1.25 ^a
I[123-cd]P	4.66 (2.42)	4.48 ^a
DB[ah]A	0.67 (0.34)	0.37 ^a
B[ghi]P	10.25 (1.98)	6.04 ^a

196 ^a Compared to certified values, mass fraction (mg/kg)

197 ^b Compared to reference values, mass fraction (mg/kg)

198 BDL (Below detection limit)

199 NR (No reference)

200 Three samples of each SRM were used (each sample of 100 mg in case of SRM 1649b and
 201 30 mg in case of SRM 1650b) and analysed to verify the quantified values through the present
 202 method.

203 Tables 3 and 4 show the comparison between the mass fraction values obtained using the
 204 presented method with the certified/reference values of mass fragment found for SRM 1650b
 205 and SRM 1649b. Two oxy-PAH: 7,12-BaAQ and 5,12-NAPQ could not be detected for
 206 analysed SRM samples and were below detection limit (BDL). Only it was possible the
 207 comparison for 7,12-BaAQ because the mass fraction of this compound reported in the SRM
 208 1649b is 3.6 mg/kg.

209 **Table 4.** Average mass fraction values compared to certified/referenced concentration for SRM 1649b (standard
 210 deviations in parentheses).

Compounds	Average concentration (n=3) (mg/kg)	Certified or referenced concentration (mg/kg)
NAPH	1.15 (0.18)	1.12 ^b
ACNY	0.29 (0.05)	0.18 ^b
ACN	0.16 (0.03)	0.19 ^b
FLUO	0.16 (0.02)	0.22 ^b
9-FLUO	1.12 (0.17)	1.40 ^c
PHEN	3.71 (0.11)	3.94 ^a
ANTH	0.54 (0.04)	0.40 ^b
FANTH	3.91 (0.18)	6.14 ^a
9,10-ANTH	1.87 (0.28)	1.80 ^c
PYR	6.06 (0.79)	4.78 ^a
B[a]A	1.45 (0.08)	2.09 ^a
BFLUO	1.14 (0.09)	NR
BEZO	1.54 (0.12)	1.60 ^c
CHR	2.63 (0.076)	3.01 ^a
7,12-BaAQ	3.82 (1.49)	3.60 ^a
5,12-NAPQ	2.39 (0.33)	NR
B[cd]PYRO	21.60 (8.68)	NR
B[b]F	4.43 (0.26)	5.99 ^a
B[k]F	1.07 (0.13)	1.75 ^a
B[a]P	2.49 (1.41)	2.47 ^a
I[123-cd]P	2.50 (0.63)	2.96 ^a
DB[ah]A	0.38 (0.03)	0.29 ^a
B[ghi]P	5.66 (0.76)	3.94 ^a

211 ^a Compared to certified values, mass fraction (mg/kg)
 212 ^b Compared to reference values, mass fraction (mg/kg)
 213 ^c Compared to information values, mass fraction (mg/kg)
 214 NR (No reference)

215 Table 4 shows that the quantified amount of 9-FLUO is slightly lower and 9,10-ANTH is
 216 slightly higher, compared to the theoretical concentrations. This results are similar to those
 217 found in a previous study that analysed SRM 1649b (Albinet et al. 2006).

218 The mass fraction of PAH and oxy-PAH and the standard deviations from the SRM 1650b
 219 and 1649b, are shown in Figure 6. Error bars express the standard deviation (SD) of each
 220 quantified analyte.

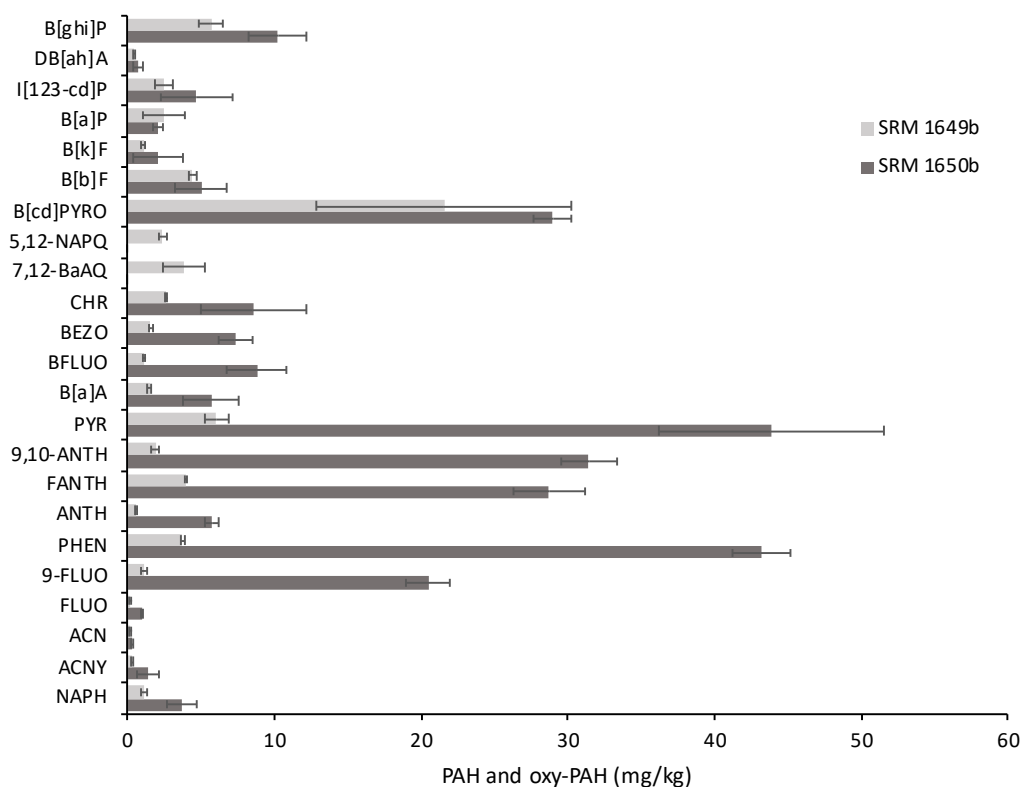


Fig. 6. Mass fraction and standard deviations of PAH and oxy-PAH from SRM 1650b and 1649b.

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223

224 Due to a lack of standard reference values, a comparison between the results obtained in
 225 different studies (Nocun and Schantz 2013; Layshock et al. 2010; O’Connell et al. 2013) was
 226 performed for validation purposes of oxy-PAH compounds. The comparison was done between
 227 studies that employed GC-MS analysis but with differences in the extraction method and
 228 chromatographic columns, Tables 5 and 6. In the present work, Soxhlet extraction was applied,
 229 while pressurized liquid extraction (PLE) was used for the rest of studies. Although PLE has
 230 higher extraction efficiencies, especially in PAH extraction from diesel particulate matter,
 231 compared to Soxhlet extraction (Schantz 2006), the present results show acceptable quantified
 232 concentrations for analysed analytes.

233 Additionally, Nocun and Schantz (2013) employed the same chromatographic column
 234 (DB17-MS) as in the present study. Nevertheless, Layshock et al. (2010) and O’Connell et al.
 235 (2013) used a DB5-MS column.

236 As it was mentioned above, two compounds (oxy-PAH) have not been detected in the
 237 present analysis. The same result was observed by Nocun and Schantz (2013), Layshock et al.
 238 (2010) and O'Connell et al. (2013) for 5,12-NAPQ in the SRM 1650b analysis.

239 The mass fraction values of oxy-PAH recovered from SRM 1649b were similar to the values
 240 obtained by other authors (Table 5). There is one exception, significant difference was obtained
 241 for values recovered for BEZO, compared with the studies done by Nocun and Schantz (2013)
 242 and Layshock et al. (2010).

243 On the other hand, the mass fraction values of 9,10-ANTH, BFLUO and BEZO from SRM
 244 1650b showed a significant difference among the compared values, except for 9-FLUO (Table
 245 6). Despite these differences, it is important to point that the values for 9-FLUO, 9,10-ANTH
 246 and BEZO were in line with the values reported for SRM 1649b. In case of B[cd]PYRO found
 247 in both samples mass fraction values were different comparing to the other authors.

248 **Table 5.** Mass fraction values reported in mg/kg for oxy-PAH from SRM 1649b.

	Present work (n=3)	Nocun and Schantz (2013) (n=3)	Layshock et al. (2010) (n=3)	O'Connell et al. (2013) (n=5)
9-FLUO	1.12	1.19	0.78	0.76
9,10-ANTH	1.87	1.39	1.60	2.6
BFLUO	1.14	1.88	1.65	0.78
BEZO	1.54	3.13	4.46	1.18
7,12-BaAQ	3.82	3.75	3.16	1.4
5,12-NAPQ	2.39	1.25	2.20	0.72
B[cd]PYRO	21.60	4.19	2.42	0.56

250 **Table 6.** Mass fraction values reported in mg/kg for oxy-PAH from SRM 1650b.

	Present work (n=3)	Nocun and Schantz (2013) (n=3)	Layshock et al. (2010) (n=3)	O'Connell et al. (2013) (n=5)
9-FLUO	20.46	25.34	24.9	19
9,10-ANTH	31.39	53.11	47.7	64
BFLUO	8.78	15.34	15.9	18
BEZO	7.34	16.03	36.9	23
7,12-BaAQ	BDL	8.9	9	5.7
5,12-NAPQ	BDL	BDL	BDL	BDL
B[cd]PYRO	28.99	5.67	9.2	5

251
 252 BDL (Below detection limit)

253

254 **4. Conclusions**

255 The present study shows a reliable and relatively simple method to identify and quantify
256 simultaneously 23 polycyclic aromatic hydrocarbons: 16 PAH and 7 oxy-PAH from different
257 samples of soot. The method involves Soxhlet extraction, concentration by rotary evaporation
258 and GC-MS analysis.

259 The repeatability of the method showed good precision using Printex-U, diesel soot
260 surrogate analysis. The present method accomplishes the objective of identification and
261 quantification of the compounds present in different SRM.

262 The mass fraction values of oxy-PAH recovered from SRM 1649b showed a good agreement
263 with the values obtained in other studies, while the values corresponding to the SRM 1650b
264 material present some differences.

265

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272

273 **Compliance with Ethical Standards**

274 **Conflict of Interest:** The authors declare that they have no conflict of interest.

275

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Joint quantification of PAH and oxy-PAH from standard reference materials (urban dust and diesel particulate matter) and diesel soot surrogate by GC-MS

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SUPPLEMENTARY MATERIAL

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1) Qualitative analysis

Table S1. Results of qualitative analysis of Printex-U, SRM 1649b and 1650b samples by GC-MS SCAN mode, 2 μ L of injection volume.

RT: Retention Time

Match: Can be defined as a factor that indicates correlation between structure of the detected compound and the compound present in the database.

Table S1. Results of qualitative analysis of Printex-U, SRM 1649b and 1650b samples by GC-MS SCAN mode, 2 μ L of injection volume.

Peak number	RT (min)	Compounds	CAS number	Match	Samples
1	10.501	cis-4,4-Dimethyl-2-pentene	000762-63-0	53	Printex-U
2	10.664	3-Methyl-1-pentene	000760-20-3	59	Printex-U SRM 1649b
3	11.758	1,1-Dichloro-2,2-dichloroethane	000079-34-5	95	Printex-U SRM 1649b SRM 1650b
4	13.993	Benzaldehyde	000100-52-7	94	Printex-U
5	14.547	Dodecane	000112-40-3	93	Printex-U
6	16.050	Benzyl alcohol	000100-51-6	96	Printex-U SRM 1650b
7	19.854	Tetradecane	000629-59-4	96	Printex-U
8	20.682	Naphthalene	000091-20-3	93	Printex-U SRM 1649b SRM 1650b
9	21.413	Benzo[c]thiophene	000270-82-6	95	Printex-U
10	21.432	2-Hydroxy-5-chlorobenzaldehyde	000635-93-8	98	SRM 1649b
11	23.257	Quinoline	000091-22-5	97	Printex-U
12	23.541	1-Methylnaphthalene	000090-12-0	96	Printex-U
13	24.318	2-Methylnaphthalene	000091-57-6	96	Printex-U
14	24.770	Heptadecane	000629-78-7	97	Printex-U
15	26.096	Biphenyl	000092-52-4	95	Printex-U
16	26.171	1,6-Dimethylnaphthalene	000575-43-9	94	Printex-U
17	26.236	1,7-Dimethylnaphthalene	000575-37-1	95	Printex-U
18	26.376	Phthalic anhydride	000085-44-9	91	Printex-U
19	26.799	2,6-Dimethylnaphthalene	000581-42-0	98	Printex-U
20	26.967	2,7-Dimethylnaphthalene	000582-16-1	97	Printex-U
21	27.502	2,3-Dimethylnaphthalene	000581-40-8	97	Printex-U
22	27.828 – 27.833	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	006846-50-0	90	SRM 1649b SRM 1650b
23	28.689	3-Methylbiphenyl	000643-93-6	94	Printex-U
24	29.043	4-Methylbiphenyl	000644-08-6	94	Printex-U
25	29.243	Acenaphthylene	000208-96-8	90	Printex-U SRM 1649b SRM 1650b

26	29.541	Octadecane	000593-45-3	97	Printex-U	SRM 1649b	SRM 1650b
27	29.974	Acenaphthene	000083-32-9	83	Printex-U	SRM 1649b	SRM 1650b
28	30.724	Dibenzofuran	000132-64-9	87	Printex-U		
29	31.487	1-Naphthalenecarbonitrile	000086-53-3	97	Printex-U		
30	31.822	2-Naphthalenecarboxaldehyde	000066-99-9	98	Printex-U		
31	31.967	1,4-Dihydro-methylethylidene-1,4-methanonaphthalene	007350-72-3	76	Printex-U		
32	32.293	Nonadecane	000629-92-5	96	Printex-U	SRM 1649b	SRM 1650b
33	32.493	2-Naphthalenecarbonitrile	000613-46-7	97	Printex-U		
34	32.847 – 32.856	Diethyl Phthalate	000084-66-2	98	Printex-U	SRM 1649b	SRM 1650b
35	33.200	Fluorene	000086-73-7	97	Printex-U	SRM 1649b	SRM 1650b
36	33.615	2-Pentadecanone, 6,10,14-trimethyl	000502-69-2	91		SRM 1649b	
37	33.764	[1,1'-Biphenyl]-4-carboxaldehyde	003218-36-8	91	Printex-U		
38	34.187	4-Methyl-dibenzofuran	007320-53-8	89	Printex-U		
39	34.271	2-phenyl-2,4,6-Cycloheptatrien-1-one	014562-09-5	86	Printex-U		
40	35.118	Dibenzo[a,e]pyran	000092-83-1	84	Printex-U		
41	35.407 – 35.440	Eicosane	000112-95-8	95	Printex-U	SRM 1649b	SRM 1650b
42	36.250	1,2-dimethyl-naphtho[2,1-b]furan	129812-23-3	74	Printex-U		
43	37.097	Acridine	000260-94-6	65	Printex-U		
44	37.469	2-[(ethylamino)methyl]-4-nitro-phenol	1000400-09-7	59	Printex-U		
45	37.688	2-[2-Phenylethenyl]phenol	042224-48-6	72	Printex-U		
46	38.098	1,2-dimethyl-naphtho[2,1-b]furan	129812-23-3	60	Printex-U		
47	38.661	4-Carbomethoxy-3-methoxy-4-methyl-2,5-cyclohexadien-1-one	120696-19-7	90	Printex-U		
48	38.954 – 38.996	n-Hexadecanoic acid	000057-10-3	98	Printex-U	SRM 1649b	SRM 1650b
49	41.338 – 41.347	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	000084-69-5	86		SRM 1649b	SRM 1650b
50	41.408	9-Fluorenone	000486-25-9	95	Printex-U	SRM 1649b	SRM 1650b
51	41.566	Dibenzothiophene	000132-65-0	95	Printex-U		
52	41.952	Naphtho[1,2-b]thiophene	000234-41-3	97	Printex-U		

53	42.781 – 42.790	Docosane	000629-97-0	96		SRM 1649b	SRM 1650b
54	43.084	Phenanthrene	000085-01-8	78	Printex-U	SRM 1649b	SRM 1650b
55	43.223	Anthracene	000120-12-7	95	Printex-U	SRM 1649b	SRM 1650b
56	43.633	Naphtho[2,1-b]thiophene	000233-02-3	96	Printex-U		
57	44.247	Benzo[h]quinoline	000230-27-3	95	Printex-U		
58	44.811	Acridine	000260-94-6	95	Printex-U		
59	45.062	Dibenzothiophene	000132-65-0	93	Printex-U		
60	45.332	3-Methyldibenzothiophene	016587-52-3	97	Printex-U		
61	45.630	9-Ethenyl anthracene	002444-68-0	96	Printex-U		
62	46.231 – 46.240	Dibutyl phthalate	000084-74-2	96	Printex-U	SRM 1649b	SRM 1650b
63	46.314	Tetraethyl pyrazine	038325-19-8	64	Printex-U		
64	46.519	Benzo[f]isoquinoline	000229-67-4	91	Printex-U		
65	46.771	Anthrone	000090-44-8	93	Printex-U		
66	46.938	2,6,10-trimethyl tetradecane	014905-56-7	91		SRM 1649b	
67	46.952	Octacosane	000630-02-4	91	Printex-U		SRM 1650b
68	47.166	1-Methylphenanthrene	000832-69-9	96	Printex-U		
69	47.245 – 47.250	Octadecanoic acid	000057-11-4	99		SRM 1649b	SRM 1650b
70	47.450 – 47.501	Naphthalic anhydride	000081-84-5	96	Printex-U		SRM 1650b
71	47.674 – 47.702	3-Methylphenanthrene	000832-71-3	94	Printex-U		SRM 1650b
72	47.916	2-Methylanthracene	000613-12-7	90	Printex-U		
73	48.349	1-Phenanthrenol	002433-56-9	90	Printex-U		
74	48.609	6-Cyclohexylnonadecane	1000357-25-3	91			SRM 1650b
75	49.145	1a,9b-dihydro-1H-Cyclopropa[l]phenanthrene	000949-41-7	96	Printex-U		
76	49.457	Naphtho[2,3-b]norbornadiene	107426-38-0	90	Printex-U		
77	51.291 – 51.314	Tetracosane	000646-31-1	98		SRM 1649b	SRM 1650b
78	51.337	2-Phenylnaphthalene	000612-94-2	97	Printex-U		
79	51.524	1,2-Acenaphthylenedione	000082-86-0	98	Printex-U		

80	52.180	1-Docosene	001599-67-3	95		SRM 1649b
81	52.189	Cyclotetracosane	000297-03-0	96		SRM 1650b
82	52.329	2,7-dimethylphenanthrene	001576-69-8	95	Printex-U	
83	52.511 – 52.557	1H-Phenalen-1-one	000548-39-0	94	Printex-U	SRM 1650b
84	53.069	Anthralin	001143-38-0	59	Printex-U	
85	53.097	n-Heptadecylcyclohexane	019781-73-8	93		SRM 1650b
86	53.479	4-Hydroxy-9-fluorenone	001986-00-1	93	Printex-U	
87	53.484	3,6-Dimethylphenanthrene	001576-67-6	62		SRM 1650b
88	54.037	1,7-Dimethylphenanthrene	000483-87-4	95	Printex-U	
89	54.270 – 54.321	9,10-Anthraquinone	000084-65-1	98	Printex-U	SRM 1649b SRM 1650b
90	55.420 – 55.425	Pentacosane	000629-99-2	91		SRM 1649b SRM 1650b
91	55.797	5,6-Dihydro-4H-benz[de]anthracene	004389-09-7	58	Printex-U	
92	56.212	2,4-Diamino-6-[3,4-dichlorophenyl]-5-methylthieno[2,3-d]pyrimidine	042160-12-3	60		SRM 1649b
93	57.185 – 57.408	Fluoranthene	000206-44-0	96	Printex-U	SRM 1649b SRM 1650b
94	57.780	Cyclopenta(def)phenanthrenone	005737-13-3	98	Printex-U	
95	57.990	1,2,3,6,7,8-Hexahdropyrene	001732-13-4	70	Printex-U	
96	58.069	4-Phenylpyridine	000939-23-1	35		SRM 1649b
97	58.763	1,1'-(1,3-butadiyne-1,4-diyl)bisbenzene	000886-66-8	68	Printex-U	
98	58.842	Benzo[b]naphtho[2,3-d]furan	000243-42-5	87	Printex-U	
99	59.191	9-Anthracenecarbonitrile	001210-12-4	94	Printex-U	
100	59.219	Hexacosane	000630-01-3	94		SRM 1649b
101	59.847	Phenaleno[1,9-bc]thiophene	079965-99-4	90	Printex-U	
102	60.015 – 60.313	Naphthalic anhydride	000081-84-5	98	Printex-U	SRM 1650b
103	60.313	Valerenic acid	003569-10-6	90		SRM 1649b
104	60.527 – 60.732	Pyrene	000129-00-0	95	Printex-U	SRM 1649b SRM 1650b
106	61.011	2,10-Dimethyl-2,3,4,5,6,7-hexahydro-1H-2-benzazonine	077581-13-6	86	Printex-U	
107	61.519	11H-Benzo[a]fluorene	000238-84-6	93	Printex-U	

108	61.691	Pyrene, 1-methyl-	002381-21-7	92	Printex-U		
109	61.868 – 61.877	cis-9,10-Octadecenoamide	000301-02-0	99	Printex-U	SRM 1649b	SRM 1650b
110	62.217	Benzo[b]naphtho[2,3-d]furan	000243-42-5	91	Printex-U		
111	62.734	Heptacosane	000593-49-7	85		SRM 1649b	
112	63.241	2-Methylpyrene	003442-78-2	89	Printex-U		
113	63.367	2-Methylfluoranthene	033543-31-6	83	Printex-U		
114	63.530 – 63.586	Methyl dehydroabietate	001235-74-1	89	Printex-U		SRM 1650b
115	63.855	Mitotane	000053-19-0	93	Printex-U		
116	64.773	4-Methylpyrene	003353-12-6	96	Printex-U		
117	65.992	Octacosane	000630-02-4	99		SRM 1649b	
118	66.104	11H-Benzo[b]fluorene	000243-17-4	70	Printex-U		
119	67.133 – 67.147	Bis(2-ethylhexyl) phthalate	000117-81-7	99	Printex-U	SRM 1649b	SRM 1650b
120	69.065	Nonacosane	000630-03-5	94		SRM 1649b	
121	69.121	4,4'-Biphenyldicarboxaldehyde	000066-98-8	41	Printex-U		
122	69.414	11H-Isoindolo[2,1-a]benzimidazol-11-one	002717-05-7	59	Printex-U		
123	70.317	1,2'-Binaphthalene	004325-74-0	96	Printex-U		
124	70.401	Benzo[fluorenone	000479-79-8	98	Printex-U	SRM 1649b	SRM 1650b
125	71.085	Benzo[b]naphtho[2,3-d]thiophene	000243-46-9	98	Printex-U		
126	71.188	5,6-Dihydro-6-oxodibenzo(b,f)-1,4-thiazepine	003159-07-7	64	Printex-U		
127	71.732	Cyclopenta[cd]pyrene	027208-37-3	95	Printex-U		
128	72.719	3-Chloro-5H-dibenz[b,f]azepine	039607-90-4	59	Printex-U		
129	72.845	7H-Benz[de]anthracen-7-one	000082-05-3	94	Printex-U		
130	73.627	Benz[a]anthracene	000056-55-3	96	Printex-U	SRM 1649b	SRM 1650b
131	74.404	3,4-Dihydrocyclopenta(cd)pyrene	025732-74-5	95	Printex-U		
132	74.511	Chrysene	000218-01-9	89	Printex-U	SRM 1649b	SRM 1650b
133	74.619	9,10-o-Benzoanthracene	000477-75-8	89	Printex-U		
134	74.702	Hentriacontane	000630-04-6	96		SRM 1649b	

135	74.861	N-phenylthiazolo[4,5-c]pyridin-2-amine	1000400-95-0	50	Printex-U		
136	75.089	9-Phenylanthracene	000602-55-1	95	Printex-U		
137	76.132	3,3,5,5-Tetramethyl-2,3,5,6-tetrahydro-S-indacene-1,7-dione	055591-17-8	58	Printex-U		
138	77.370	Benzanthrone	000082-05-3	96	Printex-U	SRM 1649b	SRM 1650b
139	78.701	2-phenylphenanthrene	004325-77-3	86	Printex-U		
140	79.656	2,2'-Binaphthalene	000612-78-2	95	Printex-U		
141	79.888	Benz(a)anthracene-7,12-dione	002498-66-0	83	Printex-U	SRM 1649b	SRM 1650b
142	83.748	Naphthacene-5,12-dione	001090-13-7	83	Printex-U	SRM 1649b	
143	86.001	1,2-Diphenyl-3-chlorocarbonyl-cyclopropene	006415-58-3	53		SRM 1649b	
144	86.033	Benzo[b]fluoranthene	000205-99-2	99	Printex-U	SRM 1649b	SRM 1650b
145	86.322	Benzo[k]fluoranthene	000207-08-9	97	Printex-U	SRM 1649b	SRM 1650b
146	86.760	Perylene	000198-55-0	95	Printex-U		
147	87.044	Aceanthrenequinone	006373-11-1	42	Printex-U		
148	87.667	4,5-Dihydrobenzo[a]pyrene	57652-66-1	78	Printex-U		
149	90.689	Benzo[a]pyrene	000050-32-8	96	Printex-U	SRM 1649b	SRM 1650b
150	91.354	Benzo[e]pyrene	000192-97-2	98	Printex-U		
151	92.993	Benzo[j]fluoranthene	000205-82-3	96	Printex-U		
152	93.105	Benzo[cd]pyrenone	003074-00-8	96	Printex-U	SRM 1649b	SRM 1650b
153	98.700	Biacenaphthenylidene	002435-82-7	55	Printex-U		
154	104.510	Indeno[1,2,3-cd]pyrene	000193-39-5	95	Printex-U	SRM 1649b	SRM 1650b
155	105.474	Dibenz[a,h]anthracene	000053-70-3	38	Printex-U	SRM 1649b	SRM 1650b
156	105.972	Dibenzo[def,mno]chrysene	000191-26-4	94	Printex-U		
157	110.842	Benzo[ghi]perylene	000191-24-2	96	Printex-U	SRM 1649b	SRM 1650b