

1 **Supplementary Material for: Chemical characterization and**
2 **stable carbon isotopic composition of particulate Polycyclic**
3 **Aromatic Hydrocarbons issued from combustion of 10**
4 **Mediterranean woods**

5
6 **A. Guillon** ^{1,2}, **K. Le Ménach** ^{1,2}, **P.-M. Flaud** ^{1,2}, **N. Marchand** ³, **H. Budzinski** ^{1,2}, **E.**
7 **Villenave** ^{1,2,*}

8 [1] {CNRS, EPOC, UMR 5805, F-33400 Talence, France }

9 [2] {Univ. Bordeaux, EPOC, UMR 5805, F-33400 Talence, France }

10 [3] {Universités d'Aix-Marseille-CNRS, UMR 6264, Laboratoire Chimie Provence, Equipe
11 Instrumentation et Réactivité Atmosphérique, Marseille, 13331, France }

12 Correspondence to : E. Villenave (eric.villenave@u-bordeaux1.fr)

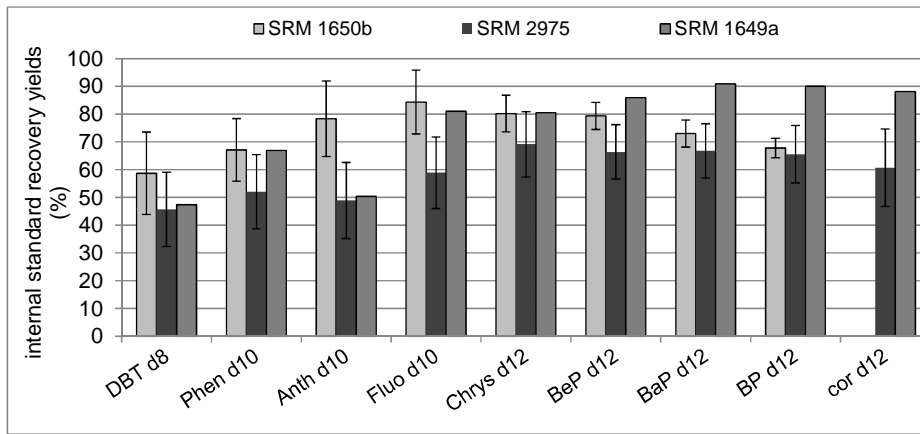
13

14 **Appendix S1: Validation of analytical procedure**

15 Firstly, SRM 2975 was extracted and particulate-PAHs were quantified with the GC/MS
16 method used for the validation of HPLC fractionation (HP-5MS column). The aims of the
17 extraction and analysis of particulate-PAHs from SRM 2975 were to confirm the good
18 internal standard recovery yields in these analytical conditions and to validate the
19 chromatographic analysis on ambient or atmospheric samples. Internal standard recovery
20 yields obtained in this work allow performing a quantification of PAHs (Fig. A1): they range
21 between $(46 \pm 13) \%$ and $(69 \pm 12) \%$ for SRM 2975. Uncertainties range from 10 to 15%,
22 traducing the complexity of natural particle composition.

23

24 Figure S1 : Internal standard recovery yields for pressurised fluid extraction of PAHs from
25 SRM 1650b, SRM 2975 and SRM 1649a

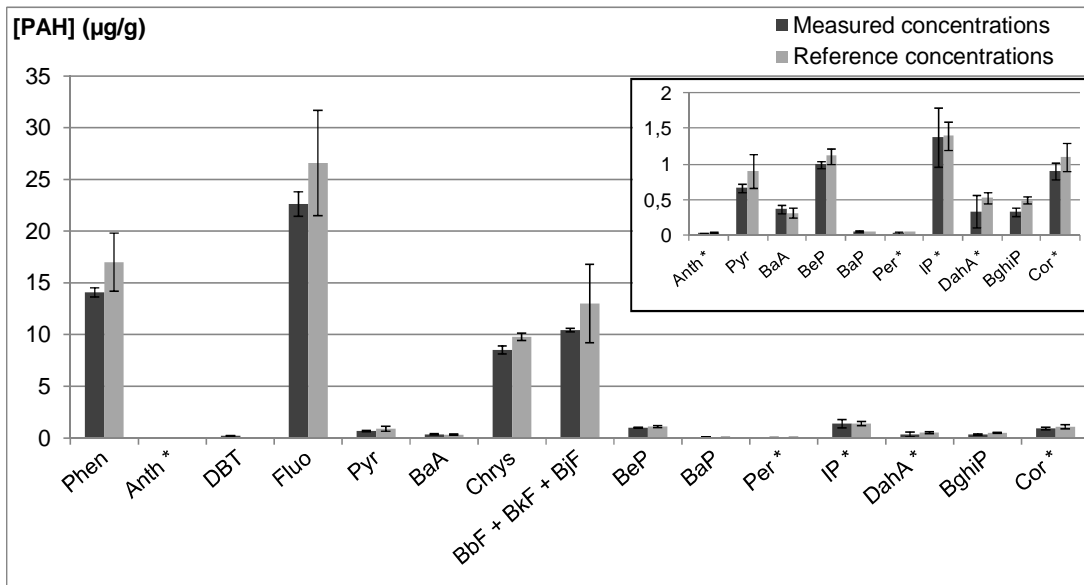


26
27

28 In this case of study, measured particulate-PAH concentrations (Fig. A2) are in good
29 agreement with PAH-certified values regardless of the compounds and the concentration
30 values.

31

32 Figure S2: Concentrations of PAHs measured in particles of SRM 2975



33

34 * PAH concentrations are not certified but only given as reference concentrations by NIST.

35

36 Note that uncertainties are low enough to precisely quantify the concentrations of PAHs
37 adsorbed on natural particles.

38

39 Therefore, in order to validate the analysis on the second chromatographic column (Rxi-17®),
40 quantification of PAHs adsorbed on particles of SRM 1650b and SRM 1649a were performed
41 in the same conditions of extraction and purification. The aims of these analyses were to
42 validate the analytical procedure (SRM1650b) and the sequence of extraction (SRM 1649a)
43 used for the particles sampled during wood combustion and extracted for the determination of
44 PAH isotopic compositions. Internal standard recovery yields allow to perform quantitative
45 measurements in accurate conditions (Fig. S1). They ranged between $(59 \pm 15) \%$ and $(84 \pm$
46 $12) \%$ for SRM 1650b and from 47 % to 91 % for SRM 1649a. Note that no uncertainties are
47 presented for SRM 1649a because only one replicate was quantified by adding this SRM with
48 the sequence of samples extraction in order to validate this series of extraction and
49 purification. Error bars obtained for SRM 1650b are between 5 and 15 % traducing the
50 complexity of natural particles, already quoted for SRM 2975. Measured concentrations of
51 SRM 1650b are in good agreement with certified and reference values (Table S1).

52

53 Most of the measured PAH concentration values are lower than those certified or referenced.
54 In this work, PFE extractions were performed at 100°C contrary to several tested conditions
55 (DCM or toluene, 100°C or 200°C) for NIST certification. Nevertheless, our set of values is
56 consistent with NIST concentrations considering reported uncertainties except for four
57 compounds. Indeed, concentrations of acenaphthylene, fluorene, anthracene and
58 dibenzothiophenes are equal or higher than the corresponding certified (or referenced) values.
59 This may be explained by the fact that these compounds were extracted by NIST at only
60 100°C (as in our study) on the contrary to other PAHs. Different certified values were
61 reported by NIST after 100°C and 200°C PFE traducing the high influence of extraction
62 conditions on PAH concentration values.

63

64 Regarding the SRM 1649a, measured values are all in good agreement with the certified
65 values reported by NIST (Table S1). The results obtained on SRM 1650b and SRM 1649a
66 traduce the good reproducibility and repeatability of our analytical procedure. Analyses
67 performed in accurate conditions were validated and consequently, allow the determination of
68 the concentrations of PAHs of generated particles.

69 Table S1: Measured concentrations ($\mu\text{g/g}$) of PAHs extracted from SRM 1650b and SRM
70 1649a

PAHs	SRM 1650b		SRM 1649a	
	Measured concentrations	Certified values	Measured concentrations	Certified values
Acy *	<i>0.35 ± 0.04</i>	<i>0.36 ± 0.03</i>		
Ace *	<i>0.12 ± 0.04</i>	<i>0.223 ± 0.024</i>		
Fl *	<i>0.83 ± 0.10</i>	<i>0.77 ± 0.04</i>	0.13	0.23 ± 0.05
Phen	61.63 ± 6.81	69.5 ± 1.9	3.54	4.14 ± 0.37
Anth	<i>2.16 ± 0.39</i>	<i>1.58 ± 0.22</i>	0.53	0.432 ± 0.082
DBT *	<i>11.39 ± 0.94</i>	<i>9.18 ± 0.43</i>	0.22	0.18 ± 0.01
Fluo	45.09 ± 1.67	47.3 ± 0.8	5.83	6.45 ± 0.18
Pyr	37.15 ± 3.49	43.4 ± 1.6	4.68	5.29 ± 0.25
BghiF **	11.13 ± 1.34	10.8 ± 1	0.91	0.88 ± 0.02
BcP **	2.79 ± 0.18	2.51 ± 0.29		
BaA	6.20 ± 0.21	6.18 ± 0.3	2.13	2.208 ± 0.073
Chrys	22.67 ± 0.80	22.47 ± 2.04	3.76	4.406 ± 0.104
CcdP *	<i>3.57 ± 0.15</i>	<i>0.35 ± 0.04</i>		
BbF	6.43 ± 0.42	6.77 ± 0.84	5.32	6.45 ± 0.64
BkF	2.16 ± 0.06	2.37 ± 0.21	1.74	1.913 ± 0.031
BjF **	2.77 ± 0.05	3.24 ± 0.42	1.75	1.5 ± 0.4
BaF	0.33 ± 0.03	0.37 ± 0.029	0.55	0.409 ± 0.035
BeP	5.58 ± 0.06	6.3 ± 0.5	3.05	3.09 ± 0.19
BaP	0.76 ± 0.06	1.17 ± 0.09	2.02	2.509 ± 0.087
Per	0.06 ± 0.01	0.165 ± 0.032	0.61	0.646 ± 0.075
DBacA	0.39 ± 0.02	0.438 ± 0.043	0.42	0.2 ± 0.025
IP	2.55 ± 0.18	4.44 ± 0.28	2.53	3.18 ± 0.72
DBahA	0.32 ± 0.01	0.365 ± 0.071	0.34	0.288 ± 0.023
BghiP	3.95 ± 0.35	5.91 ± 0.18	3.88	4.01 ± 0.91
Anth			0.69	0.45 ± 0.067
DBbkF			0.76	0.724 ± 0.076
DalP *			0.07	0.0612 ± 0.007
DaeP			0.50	0.565 ± 0.06
Cor *			3.70	3.59 ± 0.58
DahP			0.11	0.047 ± 0.01

71 *Concentration values for these PAHs are not certified but only given as reference
72 concentrations by NIST for these two reference materials.

73 **Concentrations for these PAHs are certified for SRM 1650b but only given as reference
74 values for SRM 1649a

75 *Italic values* correspond to concentrations validated by PFE at 100°C only

76 **Appendix S2: Quality insurance**

77

78 - **Extraction blanks**

79 Therefore, PAH concentrations were determined in “extraction blank” corresponding to the
80 application of analytical procedure of preparation applied without any particles or filters.
81 These blank measurements traduce levels of PAHs that could interfere during the protocol of
82 sample preparation. No PAHs were detected except acenaphthene (< 1 ng), phenanthrene (<
83 2.5 ng), anthracene, DBT, fluoranthene and pyrene (< 0.7 ng). These values are not significant
84 compared to the quantities of PAHs extracted from the ambient samples (at least 10 times
85 higher than blanks levels).

86

87 - **Blank filters :**

88 Concentrations of PAHs were determined on the blank filters collected prior to any series
89 sampling of wood combustion. In the blanks, internal standard recovery yields are ranging
90 between 50 and 90%, depending on the sample and the PAH. These values allow performing
91 quantification in accurate conditions and levels of PAHs on blank filters were determined
92 following the validated analytical protocol described in previous sections. Most of PAHs were
93 not detected on blank filters except acenaphtylene (< 3 ng/filter), phenanthrene (< 0.5
94 ng/filter), fluoranthene (< 0.8 ng/filter), pyrene (< 1 ng/filter), benz(a)anthracene and
95 chrysene (both < 0.3 ng/filter). These values were subtracted from the masses of PAHs
96 measured on the punch, corrected with filter surface ratio.