Supplementary Material

Optimization of a low volume extraction method to determine polycyclic aromatic hydrocarbons in aerosol samples

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Table S1. Standards used for construction of the analytical curves and in the recovery tests.

Analyte standard	Details
Solutions	
Mixture of the 16 priority PAHs (naphthalene, acenaphthylene, acenaphthene, phenanthrene, anthracene, fluorene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a*,*h*]anthracene, benzo[*g*,*h*,*i*]perylene)	Supelco, 2,000 µg mL^{-1}
Mixture of 6 deuterated PAHs (1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12})	Supelco, 2,000 µg mL^{-1}
retene	SPEX CertiPrep, 1,000 µg mL^{-1}
benzo[*e*]pyrene	Sigma-Aldrich, 100 µg mL^{-1}
9-nitrophenanthrene	Dr. Ehrenstorfer GmbH, 10 µg mL^{-1}
Liquids	
acetophenone	Sigma-Aldrich, ≥ 99.5%
1-naphthaldehyde	Sigma-Aldrich, 95%
Solids	
1,4-benzoquinone	Sigma-Aldrich, > 98%
1,4-naphthoquinone	Sigma-Aldrich, ≥ 96.5%
9,10-phenanthrenequinone	Sigma-Aldrich, ≥ 99%
9,10-anthraquinone	Acros Organics, 98%
5-nitroacenaphthene	Dr. Ehrenstorfer GmbH, 96.4%
2-nitrofluorene	Sigma-Aldrich, 98%
9-nitroanthracene	Sigma-Aldrich, 93%

benzo[*a*]fluorenone	Sigma-Aldrich, solid, 99.79%
3-nitrofluoranthene	Sigma-Aldrich, 90%
1-nitropyrene	Sigma-Aldrich, ≥ 95%
6*H*-benzo[*cd*]pyren-6-one	Sigma-Aldrich, 98.8%
6-nitrobenzo[*a*]pyrene	Santa Cruz, 99.78%
fluorene-d_{10}	Sigma-Aldrich, ≥ 98%
benzo[*a*]pyrene-d_{12}	Sigma-Aldrich, ≥ 98%
9,10-anthraquinone-d_8	Santa Cruz, 97%
9-nitroanthracene-d_9	Toronto Research Chemicals, 99%
levoglucosan	Sigma-Aldrich, 99%
levoglucosan-C13	Cambridge Isotope Laboratories, 98%

Table S2. Internal standards and the corresponding analytes.

Deuterated internal standard	**Analyte**
naphthalene-d_8	naphthalene
acenaphthene-d_{10}	acenaphthylene
	acenaphthene
phenanthrene-d_{10}	phenanthrene
	anthracene
fluorene-d_{10}	fluorene
chrysene-d_{12}	fluoranthene
	pyrene
	retene
	benzo[*a*]anthracene
	chrysene
benzo[*a*]pyrene-d_{12}	benzo[*a*]pyrene
	benzo[*e*]pyrene
perylene-d_{12}	benzo[*b*]fluoranthene
	benzo[*k*]fluoranthene
	indeno[1,2,3-*cd*]pyrene
	dibenz[*a*,*h*]anthracene
	benzo[*g*,*h*,*i*]perylene
9,10-anthraquinone-d_8	acetophenone
	1-naphthaldehyde
	1,4-benzoquinone
	1,4-naphthoquinone
	9,10-phenanthrenequinone
	9,10-anthraquinone
	benzo[*a*]fluorenone
	6*H*-benzo[*cd*]pyren-6-one
9-nitroanthracene-d_9	5-nitroacenaphthene
	9-nitroanthracene
	9-nitrophenanthrene
	3-nitrofluoranthene
	1-nitropyrene
	6-nitrobenzo[*a*]pyrene
levoglucosan-C13	levoglucosan

Table S3. Selected ions for each analyte, organized by retention time.

Analyte	Quantification ion (*m/z*)	Confirmation ion (*m/z*)	Retention time (min)
1,4-benzoquinone	108	110	5.20
acetophenone	105	77	5.43
naphthalene-d_8	136	134	6.23
naphthalene	128	127	6.25
1,4-naphthoquinone	158	130	7.56
acenaphthylene	152	151	7.86
acenaphthene-d_{10}	164	162	8.03
acenaphthene	154	153	8.08
1-naphthaldehyde	156	127	8.22
fluorene-d_{10}	176	175	8.80
fluorene	166	165	8.86
9,10-phenanthrenequinone	180	208	10.50
phenanthrene-d_{10}	188	189	11.09
phenanthrene	178	176	11.17
anthracene	178	176	11.33
9,10-anthraquinone-d_8	216	188	14.14
9,10-anthraquinone	180	208	14.23
5-nitroacenaphthene	199	152	14.85
fluoranthene	202	101	15.93
2-nitrofluorene	165	211	16.60
pyrene	202	101	16.93
9-nitroanthracene-d_9	232	184	17.03
9-nitroanthracene	223	176	17.10
9-nitrophenanthrene	165	176	18.46
retene	219	234	18.47
benzo[*a*]fluorenone	202	230	20.99
benzo[*a*]anthracene	228	114	22.68
chrysene-d_{12}	240	236	22.73
chrysene	228	114	22.85
3-nitrofluoranthene	201	247	24.17
1-nitropyrene	201	247	25.08
benzo[*b*]fluoranthene	252	250	27.54
benzo[*k*]fluoranthene	252	250	27.64
benzo[*e*]pyrene	252	250	28.65
benzo[*a*]pyrene-d_{12}	264	260	28.76
benzo[*a*]pyrene	252	250	28.85
6*H*-benzo[*cd*]pyren-6-one	254	226	28.83
perylene-d_{12}	264	260	29.09
indeno-[1,2,3-*cd*]-pyrene	276	138	33.04
dibenzo[*a,h*]anthracene	278	139	33.14
benzo[*g,h,i*]perylene	276	138	33.91
6-nitrobenzo[*a*]pyrene	267	297; 239	33.46

Table S4. Analysis of variance for the linear regression model calculated from the mixture design experimental data.

Parameter	**SS**	**DF**	**MS**	**F_{calc}**	**$F_{critical}$ (95%)**
Regression	0.0405	2	0.0202	7.5960	4.2560
Residual	0.0240	9	0.0027		
Total	0.0644	11	0.0059		
Pure error	0.0170	2	0.0085	0.1171	19.353
Lack of fit	0.0070	7	0.0010		
R^2	0.6280				
R^2 max	0.7924				

SS = sum of squares; DF = degrees of freedom; MS = mean square.

Table S5. Analysis of variance for the linear regression model calculated from the full factorial design experimental data.

Parameter	**SS**	**DF**	**MS**	**F_{calc}**	**$F_{critical}$ (95%)**
Regression	0.0242	5	0.0048	1.6405	3.4820
Residual	0.0265	9	0.0029		
Total	0.0507	14	0.0036		
Pure error	0.0065	6	0.0011	6.1736	4.7570
Lack of fit	0.0200	3	0.0067		
R^2	0.4768				
R^2 max	0.8720				

SS = sum of squares; DF = degrees of freedom; MS = mean square.

Table S6. Limits of detection and quantification, linear working range, equation, and correlation coefficient (r) obtained for each analyte.

Analyte	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Linear working range (ng mL^{-1})	Linear equation	r
1,4-benzoquinone	5.0	-	-	-	-
acetophenone	1.0	-	-	-	-
naphthalene	1.0	-	-	-	-
1,4-naphthoquinone	5.0	-	-	-	-
acenaphthylene	1.0	-	-	-	-
acenaphthene	1.0	-	-	-	-
1-naphthaldehyde	5.0	-	-	-	-
fluorene	1.0	10	10 - 500	y = 5.828x - 0.0195	0.998
9,10-phenanthrenequinone	1.0	10	10 - 500	y = 1.293x + 0.0017	0.992
phenanthrene	1.0	10	10 - 500	y = 4.5766x + 0.1172	0.998
anthracene	1.0	10	10 - 500	y = 4.886x + 0.0039	0.991
9,10-anthraquinone	1.0	10	10 - 500	y = 6.976x + 0.0092	0.999
5-nitroacenaphthene	10	50	50 - 500	y = 2.862x - 0.0015	0.995
fluoranthene	1.0	10	10 - 500	y = 4.9538x + 0.0152	0.994
2-nitrofluorene	10	10	10 - 500	y = 2.328x + 0.0187	0.997
pyrene	1.0	10	10 - 500	y = 5.3618x + 0.0131	0.995
9-nitroanthracene	5.0	10	10 - 500	y = 4.7736x + 0.0084	0.999
9-nitrophenanthrene	5.0	10	10 - 500	y = 0.4984x + 0.1467	0.990
retene	1.0	10	10 - 500	y = 3.2023x + 0.0094	0.999
benzo[*a*]fluorenone	1.0	10	10 - 500	y = 11.055x - 0.0511	0.999
benzo[*a*]anthracene	1.0	10	10 - 500	y = 6.33x + 0.0107	0.999
chrysene	1.0	10	10 - 500	y = 6.4523x + 0.0152	0.999
3-nitrofluoranthene	10	10	10 - 500	y = 0.6865x + 0.0046	0.997
1-nitropyrene	10	10	10 - 500	y = 0.5846x - 0.0005	0.998
benzo[*b*]fluoranthene	1.0	10	10 - 500	y = 6.8226x + 0.0128	0.999
benzo[*k*]fluoranthene	1.0	10	10 - 500	y = 9.3524x + 0.0196	0.999
benzo[*e*]pyrene	1.0	10	10 - 500	y = 6.9047x + 0.0105	0.999
benzo[*a*]pyrene	1.0	10	10 - 500	y = 6.1208x + 0.015	0.999
6*H*-benzo[*cd*]pyren-6-one	5.0	10	10 - 500	y = 45.615x - 0.1871	0.999
indeno-[1,2,3-*cd*]-pyrene	1.0	10	10 - 500	y = 6.7726x - 0.0195	0.999
dibenzo[*a*,*h*]anthracene	5.0	10	10 - 500	y = 4.3032x - 0.0156	0.999
benzo[*g*,*h*,*i*]perylene	1.0	10	10 - 500	y = 6.4871x - 0.0016	0.999
6-nitrobenzo[*a*]pyrene	10	10	10 - 500	y = 16.608x + 0.0101	0.999

Table S7. Relative standard deviations (RSDs) for the analytes determined in triplicate at three different concentrations.

Analyte	**RSD (%) (n = 3)**		
	100 ng mL^{-1}	**300 ng mL^{-1}**	**500 ng mL^{-1}**
fluorene	16	7	2
9,10-phenanthrenequinone	4	12	16
phenanthrene	5	14	5
anthracene	5	13	4
9,10-anthraquinone	7	6	6
5-nitroacenaphthene	6	8	2
fluoranthene	12	19	2
2-nitrofluorene	11	13	6
pyrene	11	19	4
9-nitroanthracene	12	4	6
9-nitrophenanthrene	7	15	7
retene	9	10	3
benzo[*a*]fluorenone	15	5	9
benzo[*a*]anthracene	9	5	3
chrysene	8	5	3
3-nitrofluoranthene	13	11	6
1-nitropyrene	12	6	10
benzo[*b*]fluoranthene	8	2	6
benzo[*k*]fluoranthene	8	3	8
benzo[*e*]pyrene	13	3	5
benzo[*a*]pyrene	8	6	5
6*H*-benzo[*cd*]pyren-6-one	11	1	10
indeno-[1,2,3-*cd*]-pyrene	4	1	8
dibenzo[*a*,*h*]anthracene	1	5	10
benzo[*g*,*h*,*i*]perylene	4	3	10
6-nitrobenzo[*a*]pyrene	15	7	2