Collection of polycyclic aromatic sulfur heterocycles from asphalt fumes and quantification by HPLC-DAD method

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SUPPLEMENTARY DATA

S1. Solvent evaporation

The PASHs standards solutions are supplied in ampules containing 100 mg L^{-1} of each compound dissolved in toluene. This solvent was partially replaced by dichloromethane to prepare PASHs stock solutions. Afterwards, the solvents toluene and dichloromethane were also evaporated under a nitrogen stream to be replaced by acetonitrile during the preparation of the PASHs working

solutions. These steps were necessary to avoid both, baseline drift and an interferent early peak related to toluene that prevents a good resolution of PASHs peaks mainly when a mix of PASHs was injected. It important to point out that the complete elimination of toluene was not necessary. A reduction of the toluene peak by 90% was enough to avoid the co-elution of the PASHs 1 and 2 (peak 0 in Figure 1) besides the baseline drift. The PASHs recoveries after these two steps of solvent replacement lie between 85.37% for Benzothiophene and 96.47% for 1,2,3,4-Tetrahydrobenzo[b]naphtho[1,2-d]thiophene.

Table S1: Resolution and selectivity for C18 and 3 PAH column.

Peak identification	Resolution		Selectivity	
	C18	3 PAH	C18	3PAH
1	11.70	14.75	3.12	2.20
2	1.33	0.86	1.07	1.02
3	0.90	1.23	1.03	1.02
4	1.13	1.84	1.04	1.04
5	9.26	0.94	1.27	1.02
6	0.93	8.13	1.02	1.20
7	5.72	1.40	1.14	1.03
8	1.27	5.61	1.04	1.10
9	1.09	1.77	1.03	1.04
10	2.58	2.04	1.05	1.04
11	1.96	0.98	1.03	1.02
12	2.94	3.69	1.05	1.08
13	1.70	1.51	1.03	1.02
14	1.08	0.74	1.02	1.01
15	1.42	2.55	1.03	1.05
16	1.33	3.70	1.02	1.06
17	1.20	1.75	1.02	1.02
18	0.84	1.39	1.01	1.01
19	2.83	1.19	1.04	1.01
20	0.84	0.63	1.01	1.00
21	6.30	5.59	1.07	1.04
22	1.86	0.57	1.02	1.00
23	3.20	2.78	1.04	1.03
24	1.60	1.54	1.02	1.02
25	1.44	2.26	1.01	1.03

26	1.10	2.71	1.01	1.02
27	10.69	0.75	1.11	1.01
28	4.36	ni	1.03	ni
29	7.40	ni	1.05	ni

ni: not identified see Figure S1.

Insert Figure S1

Table S2: Resolution using ACN and Methanol

Peak identification	Resolution	
	ACN	Methanol
1	11.56	5.52
2	10.56	8.45
3	1.15	2.39
4	1.62	2.23
5	1.00	4.04
6	4.10	1.00
7	6.05	8.71
8	1.00	1.45
9	6.14	1.50
10	1.00	1.00
11	1.17	2.08
12	1.00	1.83
13	2.81	4.36
14	1.79	1.85
15	1.77	1.00
16	2.42	1.55
17	1.80	1.60
18	1.46	1.52
19	1.00	1.00
20	1.50	1.79
21	1.00	2.19
22	1.47	2.49

23	1.00	3.87
24	1.00	1.35
25	6.13	3.33
26	2.90	2.52
27	3.84	9.56
28	2.10	1.69
29	1.96	ni
30	1.00	ni
31	12.77	ni
32	7.40	ni

ni: not identified see Figure S2.

The values of resolution with the solvent THF were not calculated because the baseline drift was high with this solvent. So, THF was not used in the sequence (See Figure S2).

Insert Figure S2

Table S3: Variation of the resolution of the compounds in relation to temperature

Peak Identification	Temperatures			
	20 °C	30 °C	40 °C	50 °C
1	11.54	10.22	10.72	7.45
2	11.82	9.88	8.75	6.56
3	1.00	1.00	1.00	1.00
4	1.00	1.00	1.44	1.81
5	1.00	1.00	7.34	7.69
6	1.00	8.81	1.00	1.00
7	8.72	1.00	4.98	6.40
8	1.00	6.39	1.45	1.65
9	5.89	1.00	1.00	1.00
10	1.20	1.21	2.39	3.44
11	1.00	1.00	1.34	1.70
12	2.02	2.56	3.89	2.83
13	3.02	1.52	1.66	1.16
14	1.92	3.18	1.27	1.68
15	2.81	1.56	1.86	1.74

16	1.33	1.59	1.00	1.00
17	1.47	1.00	1.00	1.00
18	1.64	1,.48	1.73	2.19
19	1.65	0.17	3.35	5.04
20	1.42	1.55	1.79	2.35
21	1.00	1.00	2.83	1.63
22	3.05	5.62	1.76	0.87
23	1.00	2.19	0.95	1.35
24	4.35	2.99	1.27	8.07
25	2.20	1.87	8.53	7.22
26	4.04	1.69	7.41	6.09
27	1.74	0.70	7.85	ni
28	1.24	10.14	ni	ni
29	1.09	4.82	ni	ni
30	10.57	ni	ni	ni
31	3.96	ni	ni	ni

ni: not identified see Figure S3.

With the increase in temperature, there is no identification of some peaks in the chromatographic run, indicating a greater coelution of the compounds.

Table S4: Resolutions of the compounds mentioned in Figure 3

PASHs	Resolutions			
	20 °C	30 °C	40 °C	50 °C
4,6-Diethyldibenzothiophene (24)	1.74	1.87	1.76	1.63
Cyclohexylmethyl-2-benzothiophene (25)	1.24	1.69	0.95	0.87
2,4,6,8-Tetramethyldibenzothiophene (26)	1.09	0.70	1.27	1.35

Insert Figure S3

Table S5: Recovery tests of the fortified sample AC-02

Peak Identification	PASHs	Recovery (%)
1	Benzothiophene	88.92
2	3-Methyllbenzothiophene	79.76
3	2-Methylbenzothiophene	74.82
4	2-Phenylthiophene	40.97
5	2,3-Dimethylbenzothiophene	33.07
6	2,3,7-Trimethylbenzothiophene;	34.67
7	1,2,3,4-Tetrahydrodibenzothiophene	11.79
8	2,3,4,7-Tetramethylbenzothiophene	14.28

Insert Figure S4