Supplementary Information

A novel facile method by using polyetheretherketone as a solid phase extraction material for fast quantification of urinary monohydroxylated metabolites of polycyclic aromatic hydrocarbons

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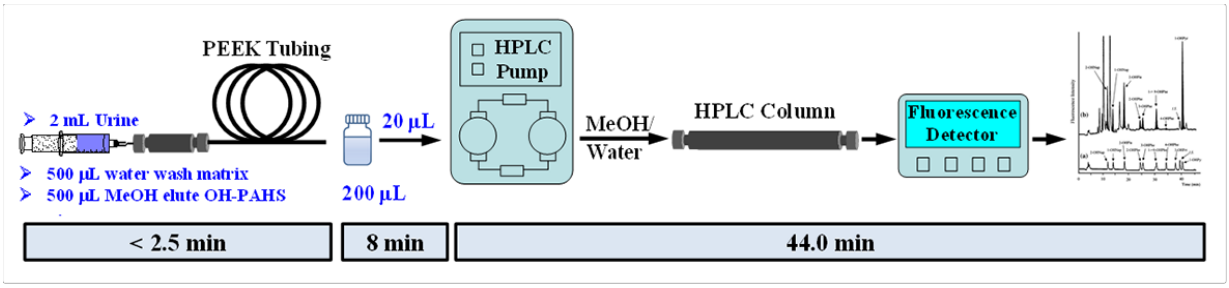

Fig. S1 Schematic diagram of the system that uses PEEK tubing for offline SPE coupled to HPLC-FD for the analysis of urinary OH-PAHs.

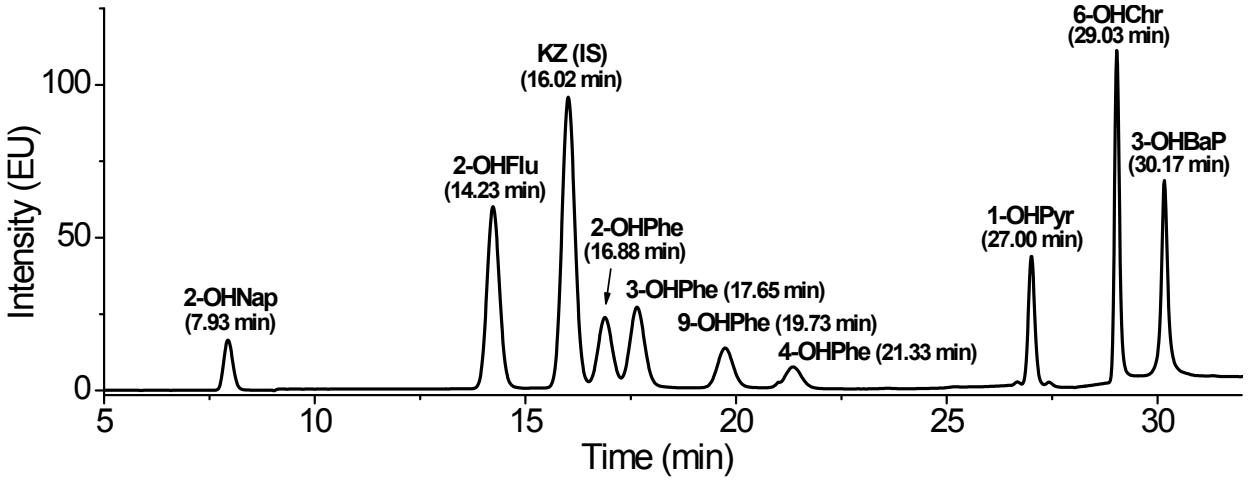

Fig. S2 HPLC chromatogram of the mixed standard solution containing 10 µg L^{-1} of OH-PAHs and 34 µg L^{-1} of KZ (IS).

Fig. S3 The commercial product of PEEK particle with an average diameter of 500 µm.

Table S1 Switching process for changing excitation and emission wavelengths (Ex/Em) to detect nine OH-PAHs and KZ (IS).

OH-PAHs	Time (min)	Ex (nm)	Em (nm)
2-OHNap	0.0–9.0	227	355
2-OHFlu	9.0–15.0	275	330
KZ, 2-/3-OHPhe	15.0–19.0	250	360
9-OHPhe	19.0–21.0	252	386
4-OHPhe	21.0–26.5	265	351
1-OHPyr	26.5–28.0	242	396
6-OHChr	28.0–29.5	262	375
3-OHBaP	29.5–44.0	368	428

Table S2 Limit of quantification (LOQ), and time and sample volume used for sample pretreatment when PEEK (this study) and C_{18} (references) are used as a SPE material, respectively.[a]

SPE material	Sources	OH-PAHs	LOQ (μg L^{-1})	Time (min)	Sample volume (mL)
PEEK (Offline)	This study	1-OHP	0.6	< 2.5	2
		3-OHBaP	0.6		
C_{18} (Offline)	Reference [1]	1-OHP	0.11	~ 30	10–15
		3-OHBaP	1.01		
C_{18} (Online)	Reference [2]	1-OHP	0.20	0.5	1

[a] HPLC-FD is used in all these methods.

Table S3 RSDs of four measurements of spiked hydrolyzed urine samples containing 0.6–50.0 μgL^{-1} of OH-PAHs.

OH-PAH	0.6 μgL^{-1}	1.0 μgL^{-1}	2.0 μgL^{-1}	5.0 μgL^{-1}	10.0 μgL^{-1}	50.0 μgL^{-1}
2-OHNap	n.a.[a]	n.a.	n.a.	14.1	17.2	4.7
2-OHFlu	n.a.	n.a.	n.a.	8.3	11.7	5.7
2-OHPhe	31.1	24.5	7.6	2.9	4.9	5.5
3-OHPhe	42.6	43.1	20.3	3.7	4.8	5.3
4-OHPhe	51.0	45.7	15.4	12.5	14.4	15.3
9-OHPhe	n.a.	n.a.	44.2	5.6	9.6	11.0
1-OHPyr	21.2	14.6	4.0	5.6	5.8	3.4
6-OHChr	33.1	27.8	3.3	6.6	11.8	5.2
3-OHBaP	7.9	9.3	9.0	13.8	12.3	16.3

[a] not available.

Table S4 Values of slope and adjusted R^2 (Adj. R^2) of linear regressions of the plots for inner diameter and length effects.

OH-PAHs	Slope (Adj. R^2)	
	ID effects	Length effects
2-OHPhe	0.0065 (0.995)	0.0019 (0.966)
3-OHPhe	0.0065 (0.994)	0.0019 (0.943)
4-OHPhe	0.0065 (0.994)	0.0018 (0.992)
9-OHPhe	0.0065 (0.985)	0.0018 (0.848)
1-OHPyr	0.0066 (0.990)	0.0020 (0.994)
6-OHChr	0.0065 (0.998)	0.0020 (0.972)
3-OHBaP	0.0062 (0.952)	0.0019 (0.906)

Table S5 Occurrence of urinary OH-PAHs in occupationally exposed workers.

OH-PAHs	Concentration (μg L^{-1})	Exposure route	Ref
2-OHNap	36.4	Coke-oven workers	[3]
	13.3	Asphalt workers/smokers	[4]
	16.8	Road construction workers/smokers	[4]
OH-Flu	9.0	Coke plant workers	[5]
2-OHPhe	15.7,	Coke plant workers	[5]
3-OHPhe	5.7	Coke-oven workers	[3]
3- and 9-OHPhe	19.2	Coke plant workers	[5]
1-OHPyr	15.4	Coke-oven workers	[3]
	7.6	Coke plant workers	[5]
3-OHBaP	161.7	Asphalt fume exposed	[6]

Table S6 Recoveries (*R*) obtained for nine OH-PAHs when PEEK particle (average diameter 500 μm) and PEEK tubing (500 μm ID) were used, respectively. [a]

OH-PAHs	*R* (%)_Particle	*R* (%)_Tubing
2-OHNap	80.9	0.3
2-OHFlu	88.2	1.0
2-OHPhe	51.3	4.3
3-OHPhe	54.8	4.1
4-OHPhe	28.9	4.6
9-OHPhe	51.4	4.1
1-OHPyr	43.5	14.4
6-OHChr	34.2	22.8
3-OHBaP	22.2	8.9

[a] It is noteworthy that further work by using this PEEK particle has not been carried out, because it is an industrial product and the particle size is not evenly distributed (Fig. S3).

References

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