Supplementary Information

Determination of 16 polycyclic aromatic hydrocarbons in tire rubber by ultra-high performance supercritical fluid chromatography combined with atmospheric pressure photoionization-tandem mass spectrometry

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Ultrasonic temperature and time were optimized in the preliminary experiment. The total amount of 16 PAHs extracted at ultrasonic temperature of 40 °C and 50 °C was similar, but in order to prevent the volatilization of some substances, we chose the ultrasonic temperature of 40 °C. The ultrasonic time was 60 min. As for ultrasonic power, the purpose of optimizing this parameter was to extract PAHs from solid samples effectively. In general, the higher the ultrasonic power, the greater the extract efficiency, however, excessive ultrasonic power led to the volatilization of PAHs such as naphthalene and increment in temperature, hence, we chose the maximum ultrasonic efficiency of 70Hz.

Figure S1 Effect of different ultrasonic temperature on the extraction of the total amount PAHs(The extraction time was 30min and the extraction solvent was ethyl acetate.)

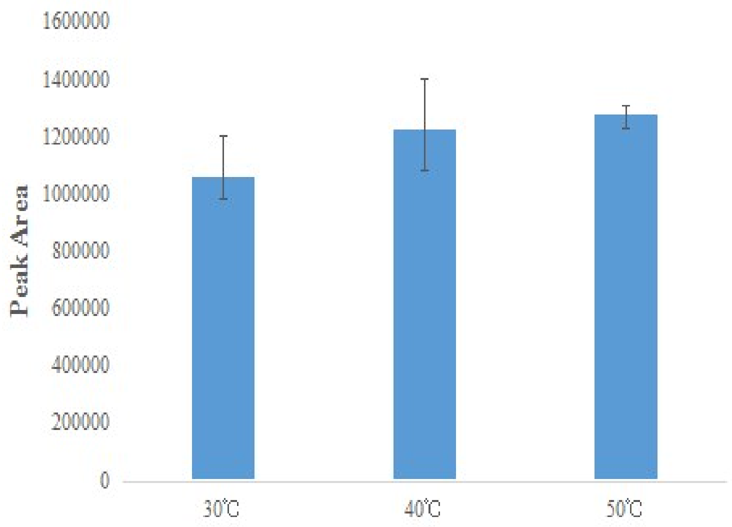


Figure S2 Effect of different ultrasonic time on the extraction of the total amount PAHs(The extraction temperature was 40 °C and the extraction solvent was ethyl acetate.)

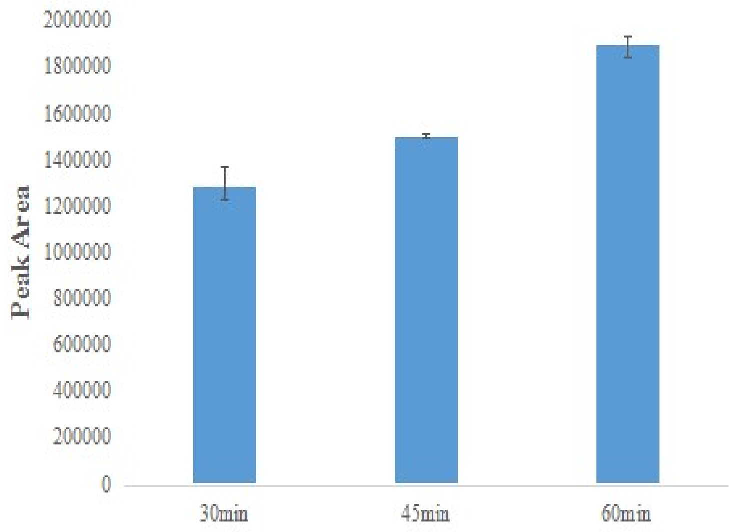
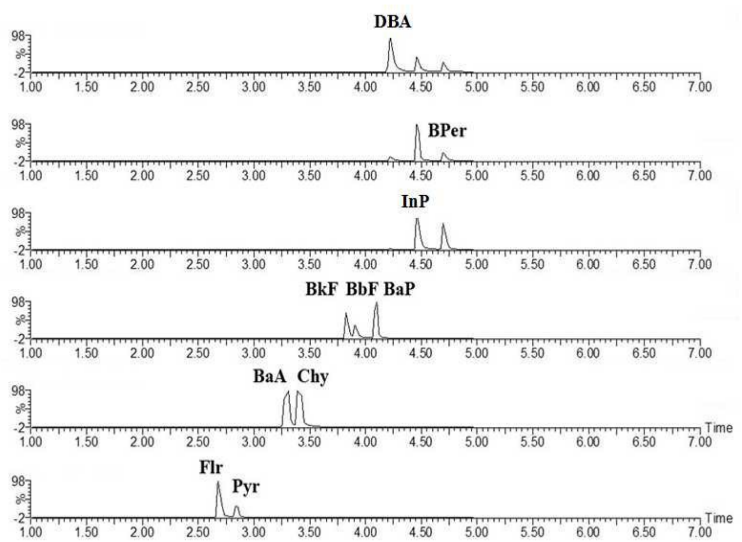


Table S1 The mass parameters of 16 PAHs

Compound	Parent(m/z)	Daughter(m/z)	Dwell(s)	Cone(V)	Collision(V)
Nap	128	102	0.04	50	22
Ace	154	127	0.04	50	30
Acpy	152	126	0.04	80	35
Flu	166	115	0.04	44	38
Ant	178	152	0.02	60	30
Phe	178	152	0.02	60	30
Fl	202	152	0.05	80	38
Pyr	202	152	0.05	80	38
BaA	228	202	0.05	75	36
Chy	228	202	0.05	75	36
BkF	252	226	0.04	48	38
BbF	252	226	0.04	48	38
BaP	252	226	0.04	48	38
DBA	278	250	0.05	80	55
InP	276	248	0.05	90	68
BPer	276	248	0.05	85	65

Figure S3 The single channel ion chromatograms of 16 PAHs on BEH 2-EP column



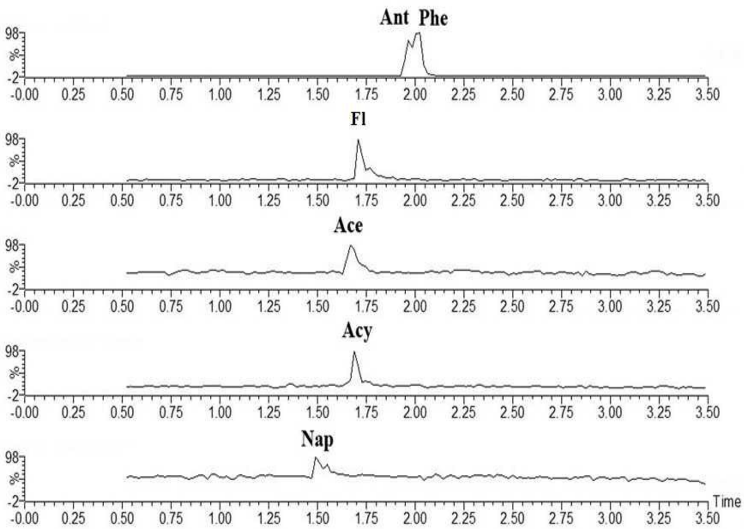


Figure S4 The single channel ion chromatograms of 16 PAHs on Torus 2-PIC column
(1) Nap; (2) Ace; (3) Acpy; (4) Flu; (5) Ant; (6) Phe; (7) Fl; (8) Pyr; (9) BaA; (10) Chy; (11) BbF; (12) BkF; (13) BaP; (14) DBA ; (15) InP; (16) BPer.

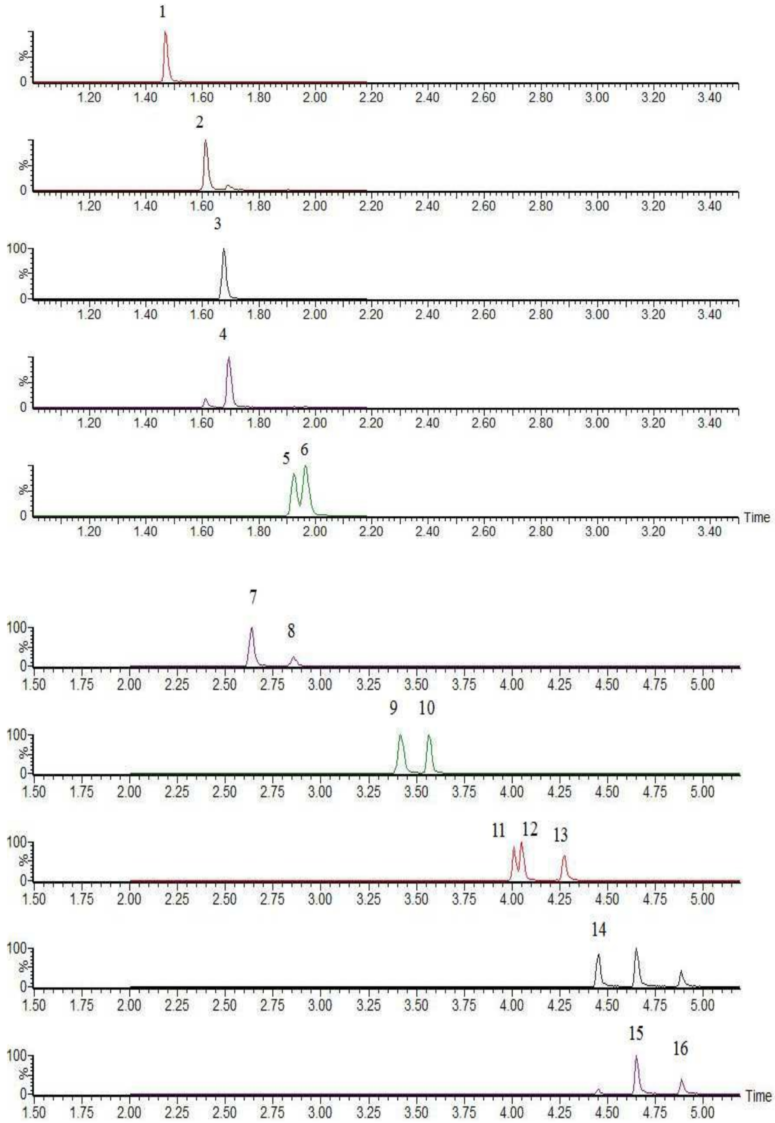


Figure S5 The chromatograms of 16 PAHs at different column temperatures

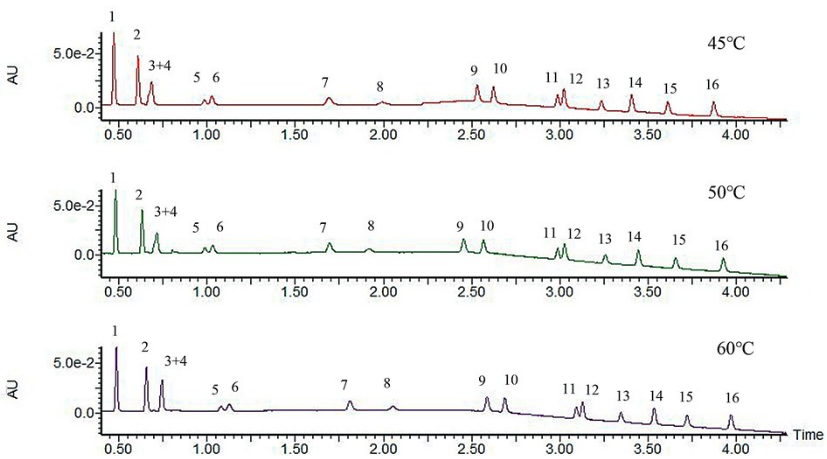


Figure S6 UHPSFC-APPI-MS/MS chromatograms of Nap and DBA in different adduct conditions

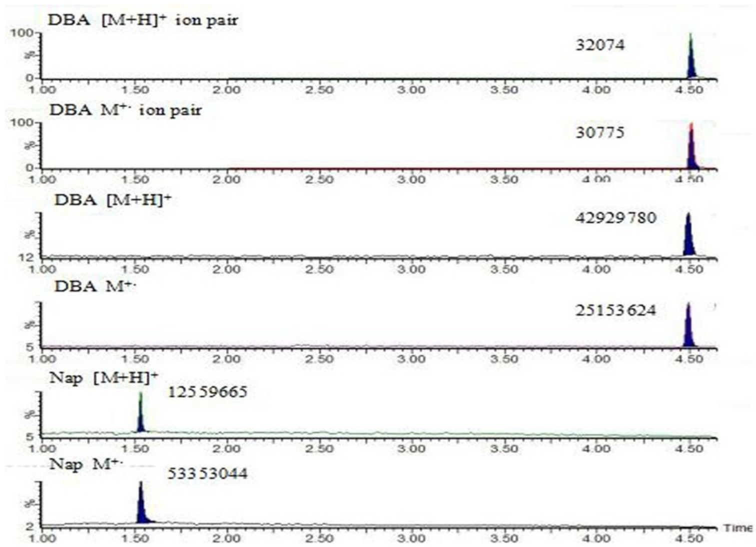


Figure S7 Effect of simple organic solvents adding to rubber sample on the extraction of PAHs (NH:n-hexane;DA2:dichloromethane/acetone(2:1);DA3:dichloromethane/acetone(3:1);DA3:dichloromethane/acetone(4:1);EA:ethyl acetate)

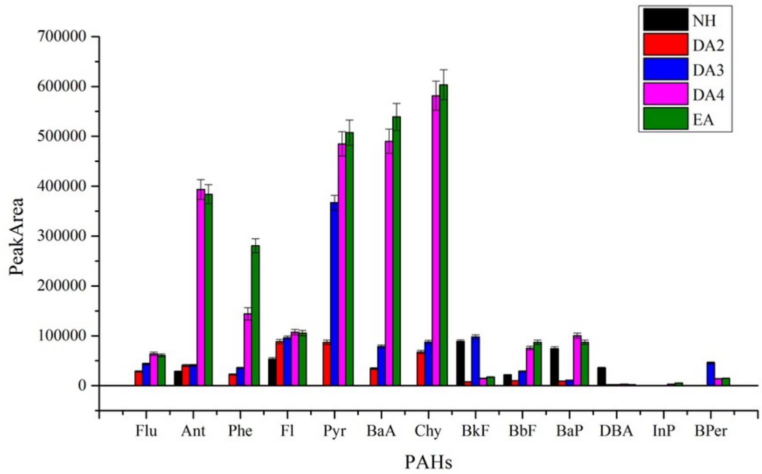


Table S2 Linear ranges, calibration curves, correlation coefficients, slope ratio of the 16 PAHs in matrix solution and acetonitrile solution analyzed by UHPSFC-APPI-MS/MS

Compound	Linear range(ng/g)	Matrix solution		Acetonitrile solution		Slope ratio
		Calibration curve	correlation coefficient(R^2)	Calibration curve	correlation coefficient(R^2)	
Nap	500-20000	Y=3.29X+949.68	0.993	Y=3.26X+901.16	0.994	100.80%
Ace	500-20000	Y=1.02X+234.67	0.992	Y=1.03X+294.04	0.993	99.42%
Acpy	500-20000	Y=0.84X+234.67	0.994	Y=0.84X+238.07	0.993	99.88%
Flu	500-20000	Y=0.84X+191.33	0.996	Y=0.84X+155.66	0.997	99.64%
Ant	500-20000	Y=6.82X-160.06	0.997	Y=0.84X+441.57	0.994	99.74%
Phe	500-20000	Y=10.68X+971.90	0.998	Y=10.69X+860.02	0.999	99.97%
Fl	500-20000	Y=3.12X+61.42	0.995	Y=3.11X+164.69	0.999	100.45%
Pyr	500-20000	Y=0.64X+192.90	0.990	Y=0.63X+196.18	0.991	101.11%
BaA	500-20000	Y=4.37X+1293.04	0.993	Y=4.37X+1294.53	0.993	99.95%
Chy	500-20000	Y=4.46X+1471.87	0.996	Y=4.48X+1513.10	0.996	99.66%
BkF	500-20000	Y=1.56X+497.96	0.992	Y=1.54X+510.07	0.992	100.84%
BbF	500-20000	Y=2.01X+524.10	0.994	Y=1.99X+547.55	0.993	101.06%
BaP	500-20000	Y=1.23X+528.05	0.993	Y=1.23X+577.77	0.993	99.43%
DBA	500-20000	Y=0.55X-18.76	0.996	Y=0.53X-16.67	0.996	104.33%
InP	500-20000	Y=0.18X-32.60	0.995	Y=0.18X-52.29	0.995	101.11%
BPer	500-20000	Y=0.22X+37.06	0.992	Y=0.22X+30.95	0.989	100.46%

Figure S8 Peak area of 16 PAHs in: sereis 1: standards at 0.5 μg/g(series 1-1:standards in acetonitrile solution; series 1-2: standards in rubber extracts); series 2: standards at 5 μg/g; series 3: standards at 10 μg/g.