

Supplementary data

Ultrasensitive determination of 39 parent and emerging halogenated polycyclic aromatic hydrocarbons in human serum

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Number of Tables: 6.

Table S1. Abbreviation of 39 parent and halogenated polycyclic aromatic hydrocarbons.

Table S2. Age, gender and lipid information of the samples.

Table S3. QA/QC experiment parameters.

Table S4. Recoveries of HPAHs in different elution solvents for Supelclean™ LC-18.

Table S5. Effects of different concentrations and volumes of IPA on the recovery of standard substances in serum.

Table S6. Purification effects of different purification columns.

Number of Figure: 1.

Figure S1. Chromatograms of all analytes in the test of purification effect of real human serum samples.

Table S1. Abbreviation of 39 parent and halogenated polycyclic aromatic hydrocarbons.

No.	HPAHs	Abbreviation	No.	PAHs	Abbreviation
1	2-BromoFluorene	2-Br-Fle	24	Naphthalene	Nap
2	3-ChloroPhenanthrene	3-Cl-Phe	25	Acenaphthylene	Acy
3	9-ChloroPhenanthrene	9-Cl-Phe	26	Acenaphthene	Ace
4/5	9-ChloroAnthracene / 2-ChloroAnthracene	9-ClAnt / 2-ClAnt	27	Fluorene	Fle
6	3-BromoPhenanthrene	3-Br-Phe	28	Phenanthrene	Phe
7/8	9-BromoPhenanthrene / 2-BromoPhenanthrene	9-Br-Phe / 2-Br-Phe	29	Anthracene	Ant
9	1-BromoAnthracene	1-Br-Ant	30	Fluoranthene	Flu
10	9-BromoAnthracene	9-Br-Ant	31	Pyrene	Pyr
11	1,4-diChloroAnthracene	1,4-Cl ₂ -Ant	32	Benz[a]anthracene	BaA
12	9,10-diChloroAnthracene	9,10-Cl ₂ -Ant	33	Chrysene	Chr
13	9,10-diChloroPhenanthrene	9,10-Cl ₂ -Phe	34	Benzo[b]fluoranthene	BbF
14	1-ChloroPyrene	1-Cl-Pyr	35	Benzo[k]fluoranthene	BkF
15	3-BromoFluoranthene	3-Br-Flu	36	Benzo[a]pyrene	BaP
16	1,8-diBromoAnthracene	1,8-Br ₂ -Ant	37	Indeno[1,2,3-cd]pyrene	InP
17	9,10-diBromoAnthracene	9,10-Br ₂ -Ant	38	Dibenz[a,h]anthracene	DahA
18	4-BromoPyrene	4-Br-Pyr	39	Benzo[ghi]perylene	BghiP
19	9,10-diBromoPhenanthrene	9,10-Br ₂ -Phe			
20	1-BromoPyrene	1-Br-Pyr			
21	7-ChloroBenz[a]anthracene	7-Cl-BaA			
22	7-BromoBenz[a]anthracene	7-Br-BaA			
23	6-ChloroBenzo[a]pyrene	6-Cl-BaP			

Table S2. Age, gender and lipid information of the samples.

gender	Sample	Age(y)	Age range (y)	Total lipid (g/L)
female	female-1	72	66-75	5.41
	female-2	70	66-75	5.46
	female-3	62	56-65	9.25
	female-4	59	56-65	8.29
	female-5	53	46-55	5.19
	female-6	46	46-55	4.93
	female-7	43	36-45	6.00
	female-8	40	36-45	5.31
male	male-1	69	66-75	5.84
	male-2	68	66-75	6.10
	male-3	61	56-65	7.32
	male-4	60	56-65	7.09
	male-5	53	46-55	5.64
	male-6	48	46-55	5.40
	male-7	39	36-45	4.67
	male-8	45	36-45	4.07

Table S3. QA/QC experiment parameters.

Compounds	Linear range (ng/mL)	R²	LOD (ng/mL)	LOQ (ng/mL)	MDL (ng/mL)
2-Br-Fle	0.1-100	0.9999	0.005	0.015	0.005
3-Cl-Phe	0.1-100	0.9992	0.002	0.008	0.004
9-Cl-Phe	0.1-100	0.9993	0.002	0.007	0.141
9-ClAnt / 2-ClAnt	0.1-100	0.9998	0.001	0.005	0.003
3-Br-Phe	0.5-100	0.9997	0.002	0.006	0.002
9-Br-Phe / 2-Br-Phe	0.5-100	0.9997	0.001	0.004	0.001
1-Br-Ant	0.5-100	0.9994	0.002	0.006	0.002
9-Br-Ant	0.1-100	0.9997	0.003	0.011	0.003
1,4-Cl ₂ -Ant	0.1-100	0.9992	0.002	0.005	0.002
9,10-Cl ₂ -Ant	0.1-100	0.9998	0.001	0.005	0.001
9,10-Cl ₂ -Phe	0.1-100	0.9996	0.001	0.003	0.003
1-Cl-Pyr	0.1-100	0.9998	0.001	0.003	0.002
3-Br-Flu	0.1-100	0.9997	0.002	0.006	0.002
1,8-Br ₂ -Ant	0.1-100	0.9997	0.002	0.008	0.002
9,10-Br ₂ -Ant	0.1-100	0.9997	0.002	0.007	0.002
4-Br-Pyr	0.1-100	0.9997	0.001	0.005	0.001
9,10-Br ₂ -Phe	0.1-100	0.9998	0.002	0.007	0.002
1-Br-Pyr	0.1-100	0.9999	0.001	0.004	0.001
7-Cl-BaA	0.1-100	0.9997	0.001	0.002	0.001
7-Br-BaA	0.1-100	0.9997	0.001	0.003	0.001
6-Cl-BaP	0.1-100	0.9997	0.001	0.003	0.001
Nap	0.5-200	1.0000	0.001	0.005	4.650
Acy	0.5-200	0.9999	0.003	0.009	0.068
Ace	0.5-200	0.9999	0.008	0.028	0.324
Fle	1-200	0.9999	0.017	0.057	1.853
Phe	0.5-200	0.9999	0.014	0.046	2.099
Ant	0.5-200	0.9998	0.019	0.063	0.086
Flu	0.5-200	0.9998	0.005	0.016	0.128
Pyr	0.5-200	0.9999	0.004	0.012	0.073
BaA	0.5-200	0.9998	0.007	0.023	0.007
Chr	0.5-200	0.9999	0.008	0.025	0.008
BbF	0.5-200	0.9999	0.009	0.029	0.009
BkF	0.5-200	0.9999	0.008	0.026	0.008
BaP	0.5-200	0.9997	0.008	0.025	0.008
InP	0.5-200	0.9999	0.011	0.035	0.011
DahA	0.5-200	0.9994	0.007	0.025	0.007
BghiP	0.5-200	0.9998	0.007	0.023	0.007

Table S4. Recoveries of HPAHs in different elution solvents for Supelclean™ LC-18.

Compounds	DCM		Hex: DCM-3:7		Hex: DCM-1:1	
	Average	RSD	Average	RSD	Average	RSD
2-Br-Fle	91.9	1.6	83.8	1.0	78.3	3.7
3-Cl-Phe	80.5	0.8	74.4	1.7	69.0	5.5
9-Cl-Phe	88.4	1.8	81.9	1.4	76.4	2.4
9-ClAnt / 2-ClAnt	91.7	1.5	86.0	1.0	82.4	2.3
3-Br-Phe	86.8	2.0	81.5	2.5	78.3	2.0
9-Br-Phe / 2-Br-Phe	88.1	2.4	83.1	2.3	78.7	2.4
1-Br-Ant	94.9	1.1	90.9	1.9	89.6	2.9
9-Br-Ant	105.7	2.7	103.4	1.7	100.1	3.2
1,4-Cl ₂ -Ant	91.3	3.9	86.6	0.9	84.6	3.0
9,10-Cl ₂ -Ant	91.2	3.9	87.4	2.4	85.8	2.7
9,10-Cl ₂ -Phe	91.8	2.8	85.2	3.3	82.8	2.8
1-Cl-Pyr	97.4	0.7	92.0	2.2	90.3	3.7
3-Br-Flu	102.1	1.3	96.7	1.9	94.7	2.1
1,8-Br ₂ -Ant	89.9	1.2	95.8	4.2	93.4	4.1
9,10-Br ₂ -Ant	80.9	4.8	93.3	4.0	90.8	1.0
4-Br-Pyr	99.1	1.1	96.0	1.9	93.6	3.2
9,10-Br ₂ -Phe	102.6	0.8	98.5	1.9	96.0	1.6
1-Br-Pyr	101.5	1.6	96.6	1.3	94.6	2.8
7-Cl-BaA	98.0	1.2	94.8	2.2	94.2	2.7
7-Br-BaA	104.0	0.3	106.4	1.7	104.2	1.5
6-Cl-BaP	93.2	1.9	94.5	1.7	96.1	1.0
Nap	140.0	10.2	80.0	8.5	65.1	4.0
Acy	73.2	3.7	55.9	2.9	46.1	6.6
Ace	76.2	3.9	57.9	4.1	49.7	5.3
Fle	140.5	8.0	94.4	2.3	84.5	6.2
Phe	139.9	1.2	119.8	3.6	112.6	3.9
Ant	89.5	4.9	88.1	1.7	82.9	5.5
Flu	86.0	0.2	82.3	1.3	79.5	0.3
Pyr	85.6	0.4	83.1	0.6	80.4	0.8
BaA	94.4	1.2	95.7	0.9	94.7	0.2
Chr	85.2	8.0	88.7	0.5	87.5	0.3
BbF	81.3	3.2	81.1	1.3	80.2	0.2
BkF	75.7	2.4	76.3	0.3	75.7	0.0
BaP	80.1	3.8	81.9	0.6	81.9	0.7
InP	86.0	4.8	100.7	2.2	100.0	1.0
DahA	79.4	4.4	106.1	2.1	104.1	0.7
BghiP	70.5	4.6	99.8	1.5	98.8	0.2

Table S5. Effects of different concentrations and volumes of IPA on the recovery of standard substances in serum.

Compounds	2ml 3%IPA		2ml 10%IPA		1ml 20%IPA	
	Average	SD	Average	SD	Average	SD
2-Br-Fle	59.2	1.3	75.3	12.4	58.0	8.9
3-Cl-Phe	56.8	38.5	70.3	15.1	50.0	8.0
9-Cl-Phe	53.0	3.0	66.9	9.1	52.7	8.3
9-ClAnt / 2-ClAnt	-	-	78.9	17.8	56.9	8.7
3-Br-Phe	-	-	77.6	15.7	55.8	9.8
9-Br-Phe / 2-Br-Phe	-	-	77.6	17.2	54.2	9.6
1-Br-Ant	-	-	85.0	17.9	68.1	5.2
9-Br-Ant	-	-	86.1	12.1	69.4	9.6
1,4-Cl ₂ -Ant	-	-	81.2	13.1	62.4	11.7
9,10-Cl ₂ -Ant	-	-	79.2	6.5	66.3	12.6
9,10-Cl ₂ -Phe	-	-	80.4	17.0	58.5	9.3
1-Cl-Pyr	-	-	81.0	14.2	62.5	11.5
3-Br-Flu	43.1	38.1	78.3	7.9	67.7	12.1
1,8-Br ₂ -Ant	67.1	5.0	82.3	11.2	67.6	12.3
9,10-Br ₂ -Ant	61.7	5.5	78.7	13.0	61.9	12.5
4-Br-Pyr	52.1	21.7	81.2	15.1	63.0	12.0
9,10-Br ₂ -Phe	72.8	26.6	81.1	13.8	64.5	11.6
1-Br-Pyr	60.4	2.5	79.3	14.8	62.4	14.7
7-Cl-BaA	71.1	1.9	82.7	11.9	66.2	11.9
7-Br-BaA	74.7	4.5	79.1	14.4	68.6	12.2
6-Cl-BaP	82.4	1.6	83.6	6.0	75.7	13.7
Nap	29.8	1.3	54.6	1.0	40.4	4.1
Acy	52.6	4.0	72.1	8.0	55.6	0.5
Ace	40.3	6.5	73.3	7.8	39.5	3.3
Fle	82.3	12.4	69.2	4.1	74.8	10.8
Phe	-	-	96.6	11.5	81.4	2.1
Ant	-	-	83.7	7.8	65.8	3.5
Flu	89.0	3.4	95.4	6.3	83.5	3.6
Pyr	56.7	2.6	78.8	3.2	53.5	5.2
BaA	87.9	8.0	109.2	3.0	85.7	6.3
Chr	71.7	2.9	104.3	4.5	80.7	6.5
BbF	81.6	2.9	95.6	6.2	80.3	7.0
BkF	80.3	2.5	94.1	8.2	79.0	7.0
BaP	81.7	1.1	86.4	3.5	81.5	8.5
InP	93.0	2.9	94.8	6.3	95.2	8.0
DahA	85.5	7.4	91.1	2.0	83.9	9.3
BghiP	84.0	23.1	90.5	1.7	100.0	11.0

Table S6. Purification effects of different purification columns.

Compounds	Florisil		LC-Si		silica gel		silica gel/alumina column	
	Average	SD	Average	SD	Average	SD	Average	SD
2-Br-Fle	59.1	11.0	65.7	3.6	62.3	8.5	83.2	9.0
3-Cl-Phe	53.2	9.9	58.8	4.6	62.4	6.9	78.9	11.9
9-Cl-Phe	55.2	10.6	61.1	4.7	68.6	5.4	79.1	3.5
9-ClAnt / 2-ClAnt	59.6	10.8	65.8	4.9	73.7	6.6	89.4	11.6
3-Br-Phe	61.7	11.6	67.2	6.1	71.8	6.3	87.0	9.8
9-Br-Phe / 2-Br-Phe	60.6	12.7	66.6	5.3	74.1	5.3	83.9	8.1
1-Br-Ant	67.4	13.8	74.5	6.4	81.7	5.7	100.0	8.4
9-Br-Ant	72.7	15.4	80.0	6.9	88.3	10.4	99.9	8.1
1,4-Cl ₂ -Ant	68.8	13.7	75.8	8.2	81.5	6.7	89.9	2.2
9,10-Cl ₂ -Ant	72.8	14.8	79.5	7.8	84.1	2.0	94.7	3.8
9,10-Cl ₂ -Phe	63.5	12.7	70.4	6.2	84.3	2.5	91.4	10.5
1-Cl-Pyr	67.1	13.4	74.3	6.5	92.0	0.0	94.6	5.1
3-Br-Flu	76.1	15.8	84.4	7.5	89.7	6.9	90.4	0.4
1,8-Br ₂ -Ant	78.3	16.5	87.0	7.8	89.3	10.6	96.4	4.0
9,10-Br ₂ -Ant	67.3	13.3	74.6	6.8	77.8	5.3	92.2	7.5
4-Br-Pyr	70.7	14.5	78.5	7.0	92.3	2.2	98.9	4.4
9,10-Br ₂ -Phe	76.1	16.5	83.5	8.3	93.2	10.0	96.2	3.8
1-Br-Pyr	70.1	14.0	78.6	7.7	92.6	2.7	93.7	8.7
7-Cl-BaA	74.6	15.4	81.4	8.0	96.6	2.8	96.1	8.3
7-Br-BaA	80.2	17.1	89.6	8.7	98.3	7.8	102.2	1.1
6-Cl-BaP	12.1	7.4	85.8	7.9	111.8	19.7	89.8	3.5
Nap	53.1	6.4	46.4	4.8	73.8	0.8	81.7	3.5
Acy	36.9	5.2	35.5	2.2	81.7	2.4	90.5	4.2
Ace	41.9	4.8	40.1	4.3	82.9	2.5	91.5	3.5
Fle	78.7	8.7	67.0	7.1	93.8	1.8	92.3	3.9
Phe	102.8	9.9	100.2	6.8	98.3	1.1	93.8	5.3
Ant	71.7	7.7	74.1	1.3	94.1	1.4	88.6	4.9
Flu	75.2	1.6	74.3	3.4	91.4	2.3	85.8	2.0
Pyr	75.0	2.2	74.9	4.0	104.3	2.3	105.4	6.3
BaA	83.8	8.3	88.1	5.6	112.3	0.3	115.7	7.9
Chr	77.6	7.8	81.2	5.9	105.7	5.0	109.2	1.4
BbF	71.7	7.7	73.7	5.7	101.7	2.5	100.1	0.4
BkF	67.4	7.0	69.1	5.3	102.7	2.6	97.4	0.3
BaP	0.7	0.5	75.0	5.9	102.1	2.0	107.4	0.0
InP	78.2	6.4	82.5	8.7	93.1	6.6	113.2	1.8
DahA	83.3	9.6	83.1	12.9	103.1	5.5	123.7	4.1
BghiP	28.8	11.6	85.4	5.3	93.3	3.8	103.0	0.6

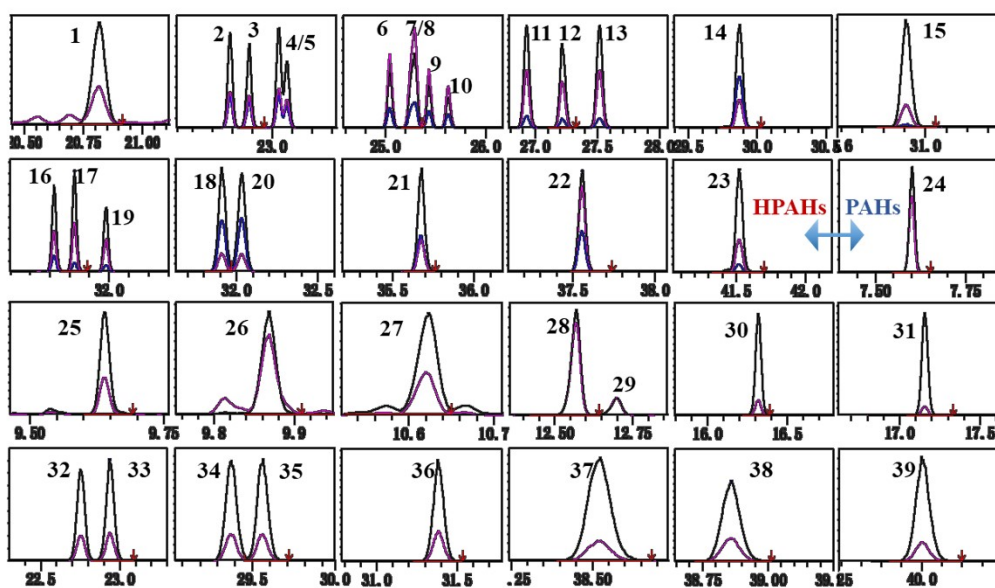


Figure S1. Chromatograms of all analytes in the test of purification effect of real human serum samples. The peak numbers and corresponding compounds were the same as those in Table 1 and Table S1.