

Supporting information for

A magnetic covalent organic framework as an adsorbent and a new matrix for enrichment and rapid determination of PAHs and their derivatives in PM_{2.5} by surface-assisted laser desorption/ionization-time of flight-mass spectrometry

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Experimental Section

Chemicals and materials

4 PAHs were purchased from Aldrich Inc., USA (biphenyl, 1 kg; pyrene, 100 g; acenaphthylene, 100 mg) and International Laboratory., USA (phenanthrene, 250 g). 4 NPAHs (1-nitronaphthalene, 3-nitrodibenzofuran, 9-nitroanthracene, 7-nitrobenz[a]anthracene) at 100 $\mu\text{g mL}^{-1}$ in toluene were purchased from AccuStandard Inc., USA. 4 OHPAHs were purchased from Dr Ehrenstorfer GmbH, Germany (2-hydroxynaphthalene, 0.5 g; 2-hydroxyphenanthrene, 10 mg), AccuStandard Inc., USA (4-hydroxybiphenyl, 100 mg) and Toronto Research Chemicals Inc., USA (3-hydroxyfluorene, 10mg).

Preparation of standard solutions

4 PAHs (biphenyl, pyrene, acenaphthylene and phenanthrene) were dissolved in n-hexane at a concentration of 100 $\mu\text{g mL}^{-1}$ as stock solutions, respectively. 4 NPAHs (1-nitronaphthalene, 3-nitrodibenzofuran, 9-nitroanthracene and 7-nitrobenz[a]anthracene) have been already in toluene at 100 $\mu\text{g mL}^{-1}$. 4 OHPAHs (2-hydroxynaphthalene, 2-hydroxyphenanthrene, 4-hydroxybiphenyl and 3-hydroxyfluorene) were prepared in acetonitrile (ACN) at a concentration of 100 $\mu\text{g mL}^{-1}$ as stock solutions, respectively.

PM_{2.5} sample collection and pre-treatment

Two parallel PM_{2.5} samples were collected at Shanxi University (37°47'42.70" N, 112°34'52.51" E) in Taiyuan, China on December 25th, 2017. Two ADS-2062E medium volume air sampler (AMAE (Shenzhen) Co., Ltd, China) and quartz

microfiber filters (Whatman, QMA, 90 mm diameter) were used for PM_{2.5} collection. The flowrate of air samplers was 0.1 m³/min and total sampling period was 23.5 h. After sample collection, the filters were wrapped with aluminum foil and sealed in zip bag at -20 °C refrigerator to prevent the photo-degradation.

The whole PM_{2.5} sample filter was cut into strips and extracted by 100 mL hexane/acetone (1:1, v/v) using ultrasonic extraction. Then the organic solvent was dried and converted into 2 mL Milli-Q water. After that, 1 mg Fe₃O₄@COFs was dispersed into the solution and sonicated for 20 min for enrichment. Next, the Milli-Q water for adsorption was wasted by magnetic separation. 1 mL new Milli-Q water was added, and solution was vortexed until homogeneous. Finally, drop 1 μL uniform sample solution on the MALDI-TOF plate and go to SALDI-TOF-MS analysis with Fe₃O₄@COFs as matrix directly. The procedures also could be seen in Scheme. S1.

Enrichment optimization

To obtain the best enrichment performance of Fe₃O₄@COFs for target PAHs and their derivatives in PM_{2.5}, different ultrasonic enrichment time and nanomaterial dosage were optimized. Mix standard of 4 PAHs, 4 NPAHs and 4 OHPAHs (10 ng for each compound) was used for optimization experiments. The results of the recoveries were determined by GC-MS. The mix standards would be treated by same sample pre-treatments procedures until magnetic separation. After magnetic separation, Fe₃O₄@COFs were extracted by dichloromethane to elute out PAHs, NPAHs and OHPAHs which were adsorbed by the nanomaterial. The extract would go to GC-MS to determine the recoveries. Both enrichment time (1 – 5 – 10 – 20 – 40

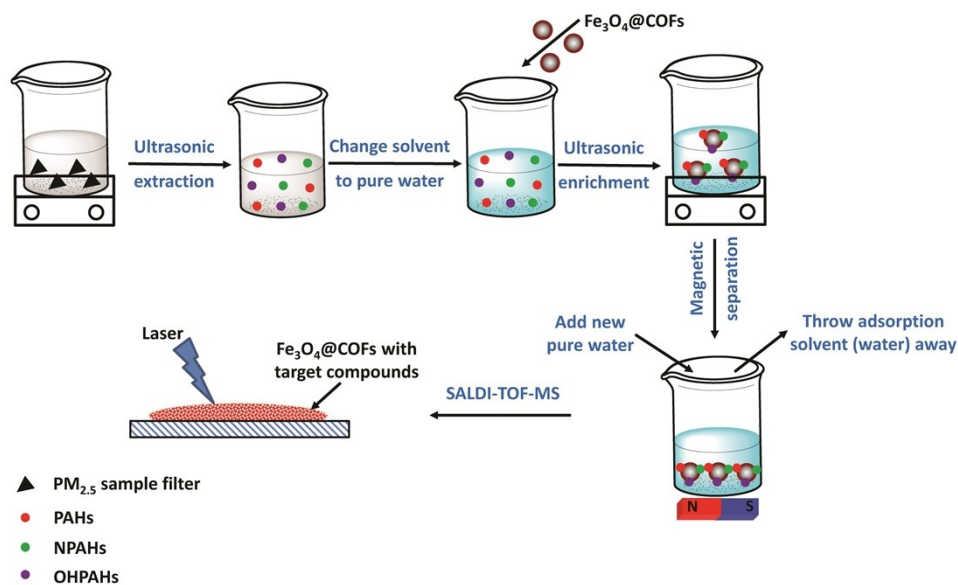
– 60 min) and Fe₃O₄@COFs dosage (0.1 – 0.25 – 0.5 – 0.75 – 1 mg) were optimized. The dosage was also associated with the SALDI-TOF-MS intensity because after enrichment Fe₃O₄@COFs would be directly used as matrix in instrumental analysis. Finally, from Fig.S2 and Fig.S3, 20 min (enrichment time) and 1 mg (Fe₃O₄@COFs dosage) were selected for enrichment.

Characterization

S-4800 TEM Scanning electron microscopy (SEM) was obtained from Hitachi, Japan. Tecnai G2 20 200 kV Transmission electron microscopy (TEM) was obtained from FEI Company (Hillsboro, OR, USA). UV-Visible spectrum was obtained by Agilent 8453 UV-Visible spectroscopy with Agilent 89090 temperature controller. Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained using Nicolet 6700 spectrometer (Thermo Fisher, USA).

Instrumental analysis

MALDI-TOF-MS analysis was performed on Bruker rapiflex MALDI TissueTyper mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen laser operated in 337 nm. PAHs were detected under positive mode. NPAHs and OHPAHs were analyzed under negative mode.



Scheme S1. Sample pre-treatment procedures using $Fe_3O_4@COFs$ as enrichment material and matrix (Detailed description was listed in “ $PM_{2.5}$ sample collection and pre-treatment” in ESI)

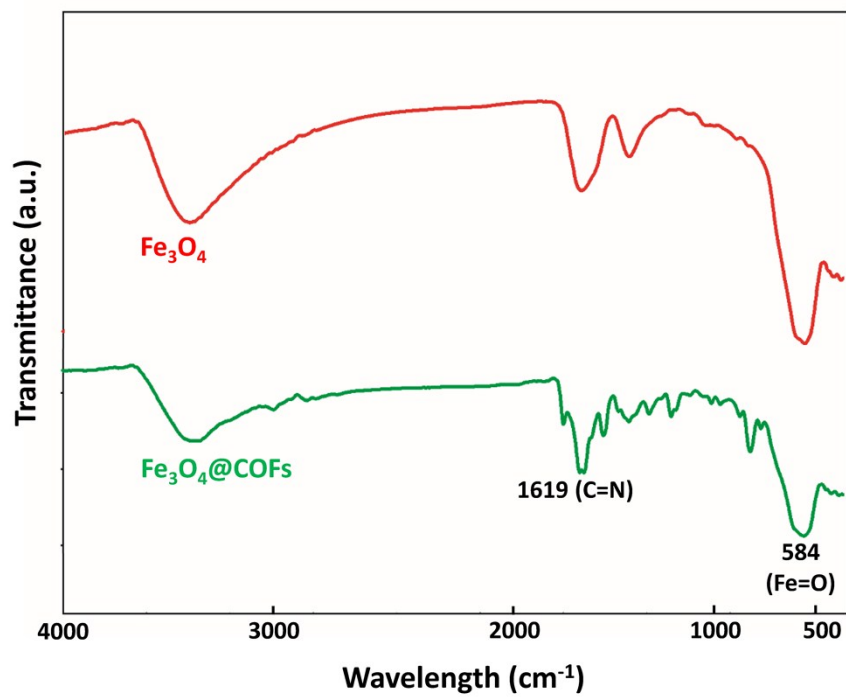


Fig.S1 FT-IR spectra of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{COFs}$

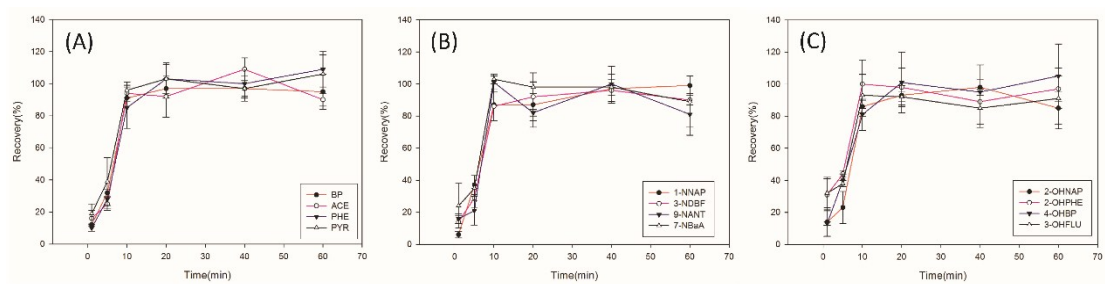


Fig.S2 Enrichment time optimization for PAHs (A), NPAHs (B) and OHPAHs (C)

with 1 mg Fe₃O₄@COFs

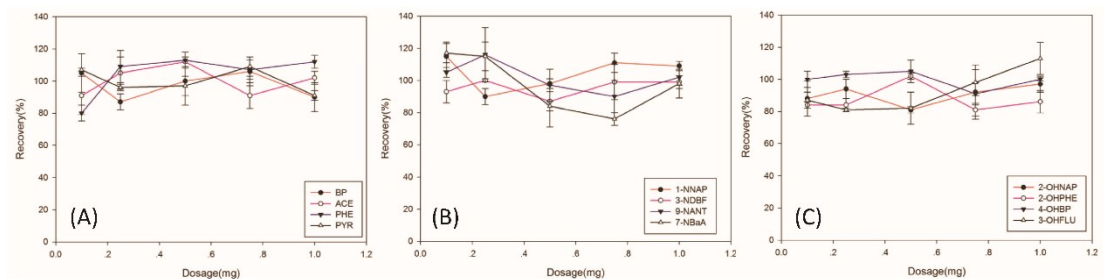


Fig.S3 Enrichment dosage optimization for PAHs (A), NPAHs (B) and OHPAHs (C)

with 20 min enrichment time

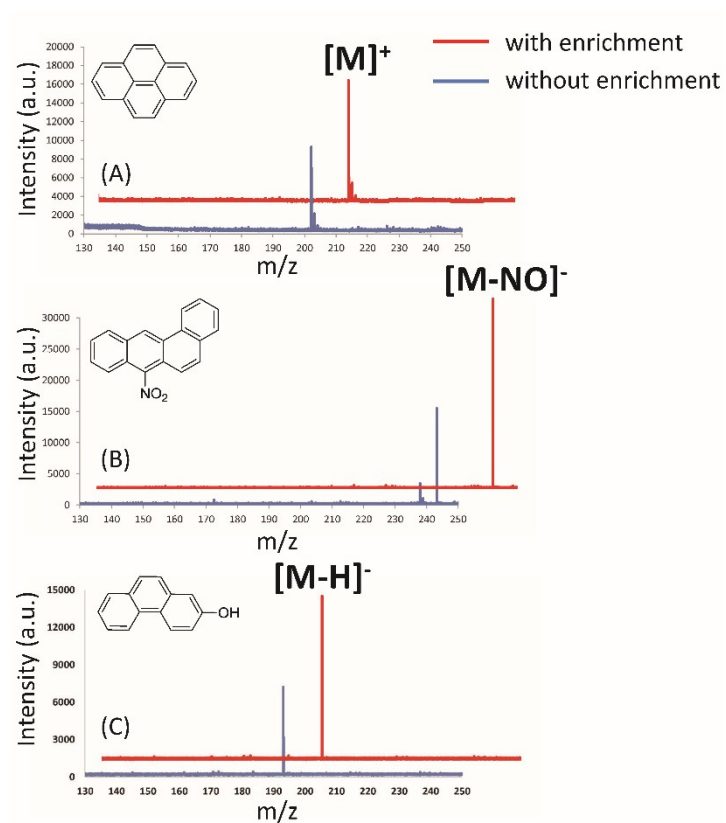


Fig.S4 Comparison of MS intensities between with and without Fe₃O₄@COFs as enrichment material to detect pyrene (A), 7-nitronitrobenz[a]anthracene (B) and 2-hydroxybiphenyl (C)

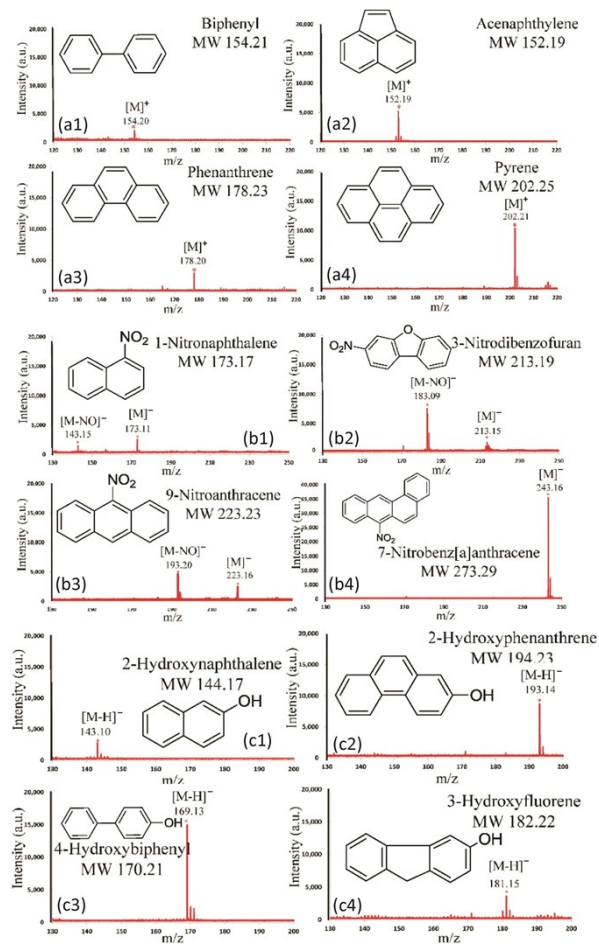


Fig.S5 SALDI-TOF-MS spectra of 4 PAHs (a1-a4), 4 NPAHs (b1-b4), and 4 OHPAHs (c1-c4)

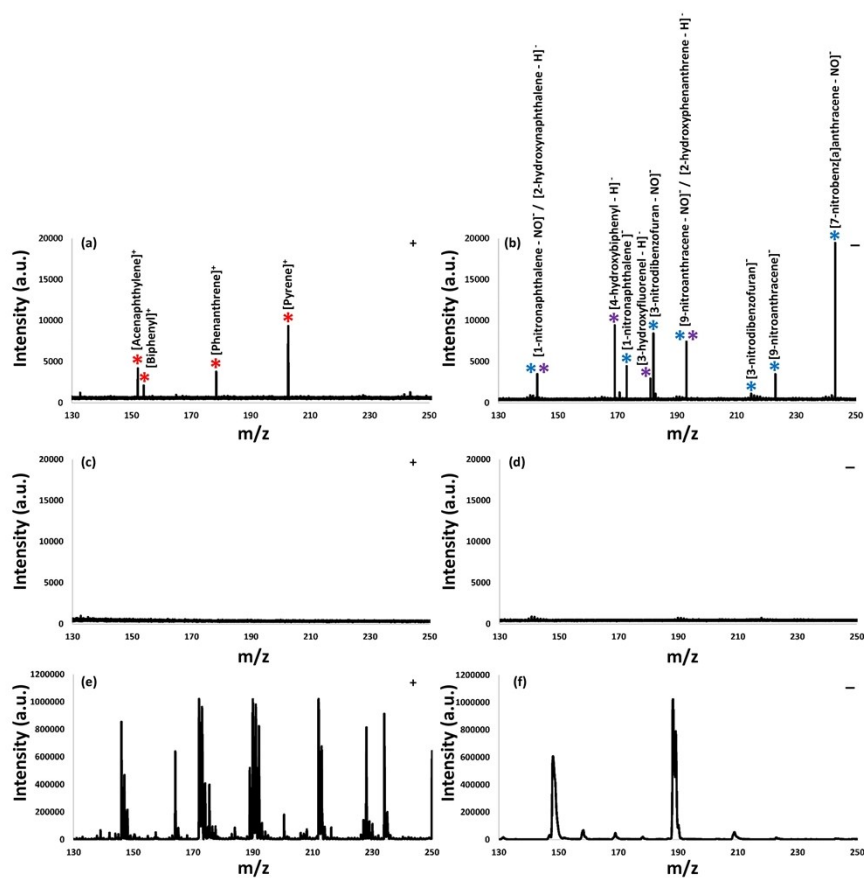


Fig.S6 SALDI-TOF-MS spectra of (a) 100 ng mix standards of PAHs in positive mode; (b) 100 ng mix standards of NPAHs/ OHPAHs in negative mode; (c) Fe₃O₄@COFs blank in positive mode; (d) Fe₃O₄@COFs blank in negative mode; (e) CHCA blank in positive mode; (f) CHCA blank in negative mode

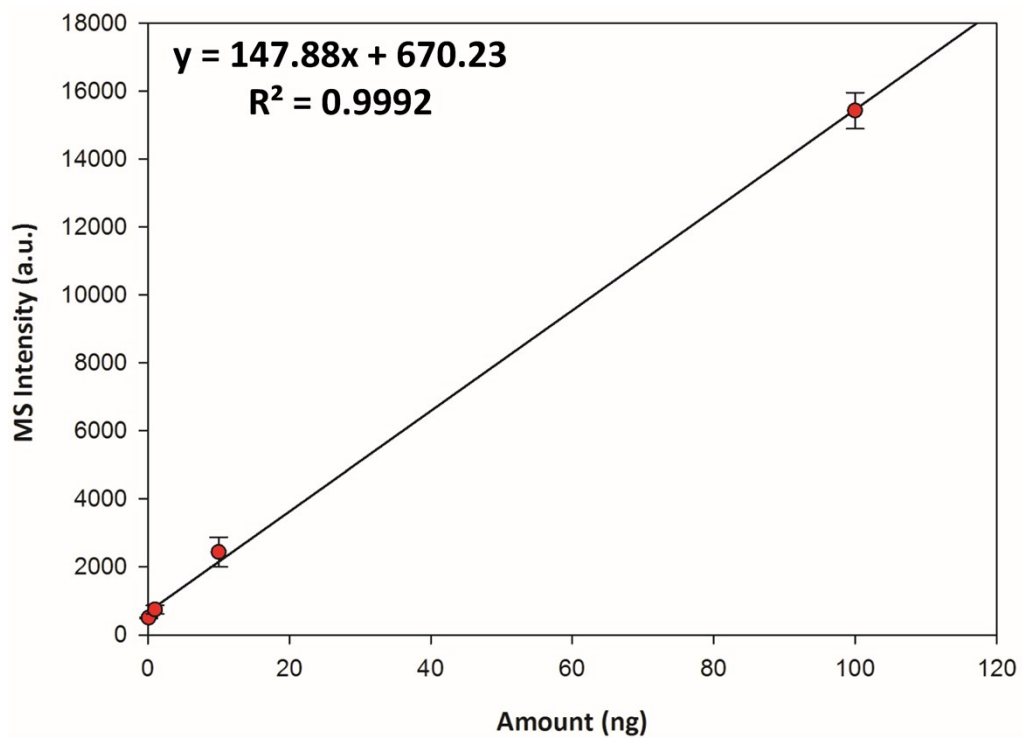


Fig.S7 Calibration curve of pyrene obtained by SALDI-TOF-MS using $\text{Fe}_3\text{O}_4@\text{COFs}$ as enrichment material and matrix simultaneously

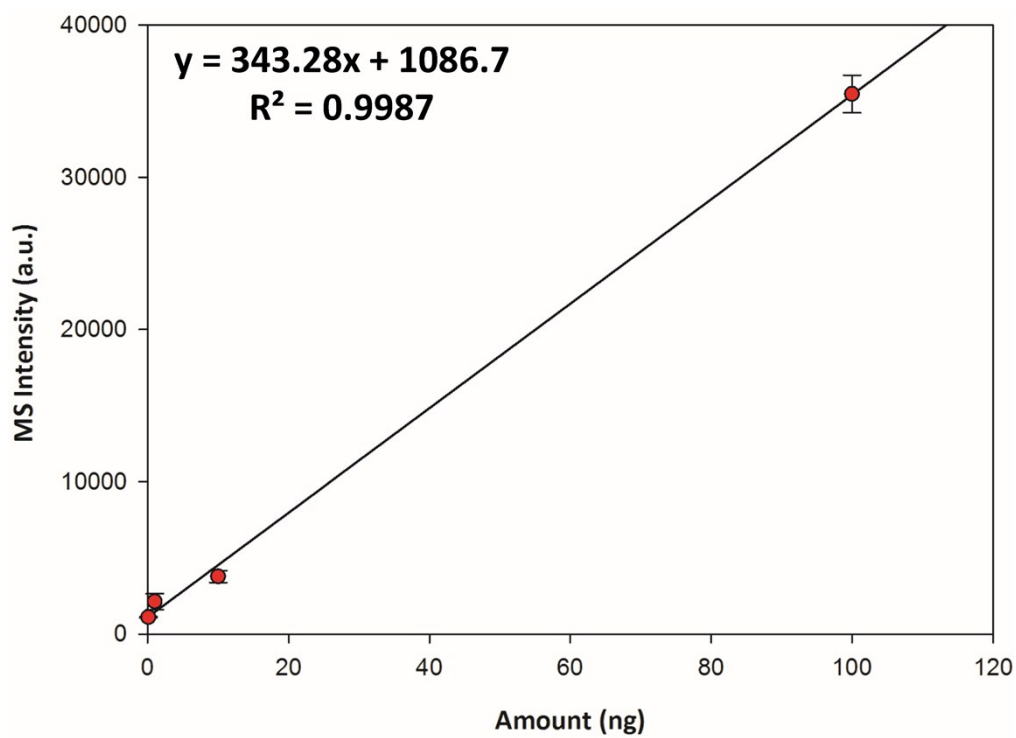


Fig.S8 Calibration curve of 7-nitrobenz[a]anthracene obtained by SALDI-TOF-MS using $\text{Fe}_3\text{O}_4@\text{COFs}$ as enrichment material and matrix simultaneously

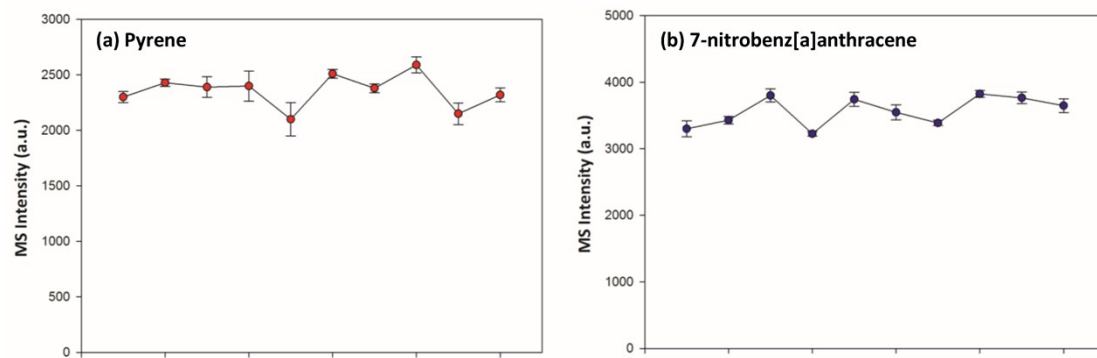


Fig.S9 Intensity reproducibilities (n=10) of 10 ng pyrene (a) in positive mode and 10 ng 7-nitrobenz[a]anthracene (b) in negative mode

Table S1. Quantification results of model compounds obtained from SALDI-TOF-MS and GC-MS

Compounds	Total amount in 1 μ L extract (SALDI-TOF-MS) / ng	Total amount in 1 μ L extract (GC-MS) / ng
Pyrene	2.37	2.62
7-nitrobenz[a]anthracene	0.11	0.07