Electronic Supporting Material

Sensitive determination of psoralen and isopsoralen in *Fructus Psoraleae* by online solid phase microextraction with porphyrin-based porous organic polymers modified on capillary

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The Electronic Supporting Material provides additional relevant details of this work, including:

- Capillary-based online SPME-HPLC for standard samples
- Optimization of synthetic conditions
- Fig. S1 Chemical structures of psoralen and isopsoralen.
- Fig. S2 Schematic of PPOPs-capillary-based online SPME-HPLC system.
- Fig. S3 XRD pattern (A) and FT-IR spectra (B) of PPOPs.
- Fig. S4 Effects of concentration of p-phthalaldehyde (A), synthetic time (B), and concentration of pyrrole (C).
- Fig. S5 SEM images of PPOPs-capillary before (A, C) and after use (B, D).
- Table S1 Enrichment factors of PPOPs-capillary for PAHs.
- Table S2 Comparison of this work and reported methods.

Capillary-based online SPME-HPLC for standard samples

The extraction capillary replaced the loop of a six-port valve on positions 1 and 4 (Supplementary material Fig. S2). Before sampling, the capillary was flushed with methanol and 10 mM phosphate buffer (pH 7) sequentially to remove the impurities and activate the column. Online SPME-HPLC was consisted of two steps. In the sample loading step, the six-port valve was set to LOAD mode and a certain volume of psoralen and isopsoralen standard solution was introduced by a syringe pump for extraction. In the eluting step, the six-port valve was switched to INJECT mode and the analytes were eluted by the mobile phase into LC column with the flow rate of 0.1 mL/min for 2 min. After elution, the six-port valve was turned to LOAD position again and the analytes were separated and analyzed by HPLC-UV at the flow rate of 1.0 mL/min. In the meantime, the capillary was flushed with methanol and phosphate buffer (pH 7) for next loading.

Optimization of synthetic conditions

P-phthalaldehyde layers were immobilized on the surface of capillary for growth of porphyrin based porous organic polymers because p-phthalaldehyde can supply aldehyde groups for growth of PPOPs. It was modified by Schiff reaction. The aldehyde groups of p-phthalaldehyde react with the amino groups of APTES in methanol solution, which produces aldehyde groups as active sites for growth of PPOPs. Therefore, as shown in Fig. S4A, different concentrations of p-phthalaldehyde varied from 1 to 4 mg/mL were investigated. The adsorption capacities of PPOPs-capillary to psoralen and isopsoralen increased gradually with the increase of the concentration of p-phthalaldehyde from 1 to 3 mg/mL. The increase of the concentration of p-phthalaldehyde can provide more effective aldehyde groups for supporting of PPOPs to some extent. When the concentration was higher than 3 mg/mL, the peak area increased slowly, indicating the almost completed reaction between the amino groups of APTES and p-phthalaldehyde. As a result, ensuring the efficient extraction, 4 mg/mL was chosen for modification.

PPOPs are modified on the inner face of CHO-terminated capillary according to Modak's method. In our work, the solution of pyrrole and p-phthalaldehyde in glacial acetic acid would turn into red color within a few minutes, indicating the feasible and quick formation of PPOPs. Therefore, appropriate synthetic time is essential for the completion of reaction. Considering the micropore of PPOPs, synthetic time should be investigated, ranging from 0.5 to 3 h. As described in Fig. S4B, the peak areas increased from 0.5 to 1 h and stabilized until 3 h. The result showed that the formation of PPOPs can be

accomplished within 1 h. Modest extension of the synthetic time is beneficial for the stability of PPOPs on the inner face of capillary. Considering the best extraction efficiency and short time-consumption, synthetic time of 2 h was selected.

Pyrrole is one of the monomer of PPOPs. Investigation of the concentration of pyrrole can increase the amount of PPOPs modified in the capillary. Thus the concentrations of pyrrole from 8.8 to 88 mM were studied. As shown in Fig. S4C, the peak areas kept an upward tendency with the increase of the concentration of pyrrole, suggesting that more PPOPs could be grown in the capillary in a higher concentration. However, when the concentration was larger than 88 mM, the capillary would sometimes be clogged. In order to obtain effective and permeable capillary, 88 mM was decided for synthesizing PPOPs.

Fig. S1 Chemical structures of psoralen and isopsoralen.

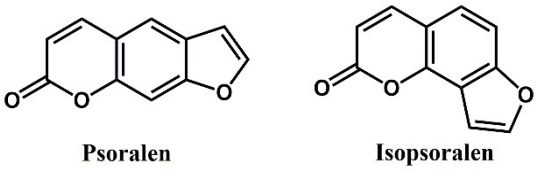


Fig. S2 Schematic of PPOPs-capillary-based online SPME-HPLC system.

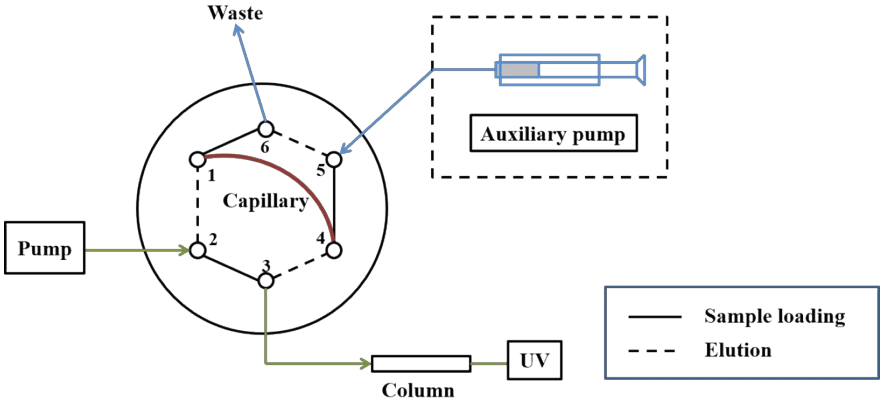


Fig. S3 XRD pattern (A) and FT-IR spectra (B) of PPOPs.

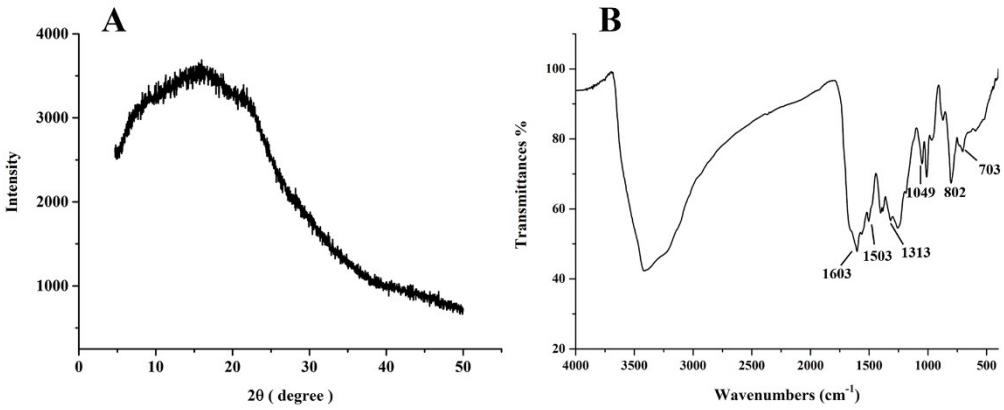


Fig. S4 Effects of concentration of p-phthalaldehyde (A), synthetic time (B), and concentration of pyrrole (C).

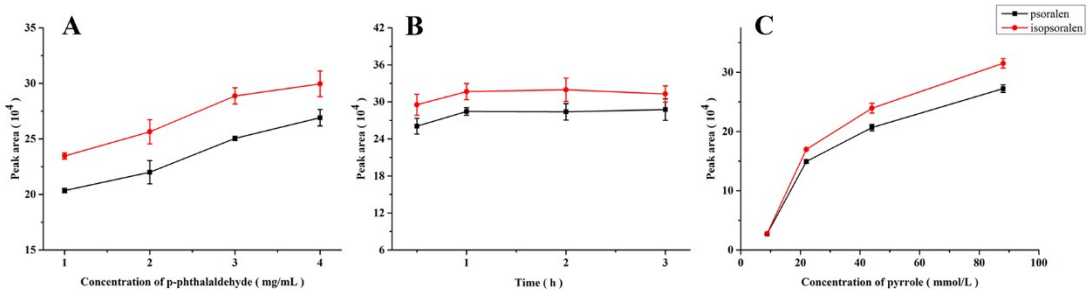
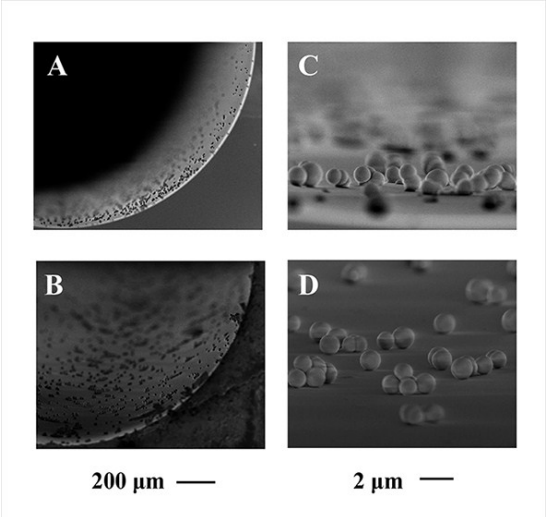
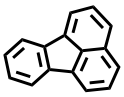
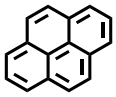
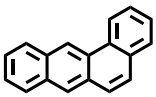
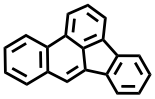
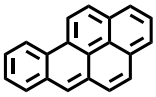
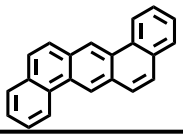


Fig. S5 SEM images of PPOPs-capillary before (A, C) and after use (B, D).



153 **Table S1** Enrichment factors of PPOPs-capillary for PAHs.

Compound	Structure	Log P	Size (Å)	EFs
Fluoranthene		5.16	9.18	150.77
Pyrene		5.05	9.23	190.72
Benz[a]anthracene		5.91	11.56	71.28
Benzo[b]fluorathene		5.78	11.41	43.54
Benzo[a]pyrene		6.35	11.49	52.06
Dibenz[a,h]anthracene		6.57	13.68	50.89

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155 **Table S2** Comparison of this work and reported methods.

Method	Extraction sorbent	Linear range (ng/mL)	LOD (ng/mL)
Solid phase extraction	Graphene-polydopamine	0.1-50	0.02
Solid phase extraction	Extraction-clean™ cartridges	0.1-3100	3.46-4.86
Solid phase extraction	MWCNT-β-CD	0.1-100	0.02
This work	PPOPs	0.05-100	0.01

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