Electronic Supplementary Information

Efficient enrichment of triazole fungicides in fruit and vegetable samples by a spherical porous aromatic framework

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S1. Experimental

S1.1. Chemicals and reagents

The six triazole fungicides standards, i.e., triadimefon (99.8%), hexaconazole (98.0%), myclobutanil (98.5%), diniconazole (99.5%), propiconazole (99.0%) and tebuconazole (99.0%) were purchased from Aladdin Chemistry (Shanghai, China). The *n*-alkanes standards including *n*-pentadecane (⩾99.5%), *n*-hexadecane (99%), *n*-octadecane (⩾99.5%) and *n*-eicosane (> 99%) were purchased from Macllin Reagent (Shanghai, China). A mixture stock solution of triazole fungicides at the concentration of 2.0 mg mL^{-1} for myclobutanil and 1.0 mg mL^{-1} for each of the others was prepared in acetone. Cyanuric chloride (99%), *p*-terophenyl (99%) and anhydrous aluminum chloride ($AlCl_3$, 99%) were purchased from Macklin Reagent (Shanghai, China). $CHCl_3$ (99%), CH_2Cl_2 (99.5%), acetone (99%), acetonitrile (99.9%), ethanol (99.7%), NaOH (96.0%) and NaCl (99.5%) were bought from Sinopharm Chemical Reagent (Shanghai, China). Neutral multifunctional silicone sealant was purchased in local building materials market (Baoding, China). The stainless steel wires (type 304, 350 μm o.d.) and GC microsyringes (5 μL) were supplied by Gaoge Industrial and Trade Co., Ltd. (Shanghai, China). The double-distilled water for the experiments was prepared on an SZ-93 automatic double-distiller system (Yarong Biochemistry Instrumental Factory, Shanghai, China).

S1.2. Instrumentals

The triazole fungicides were analyzed by a GC-MS system composed of an Agilent 7820A gas chromatography coupled with an Agilent 5977E mass spectrometric detector (Santa Clara, CA,

USA). The analytes separations were carried out on a HP-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) coated with (5%-phenyl)-methyl polysiloxane (Agilent J&W Scientific, CA, USA). GC-MS column temperature program triazole fungicides were set as follows: initial temperature was 80 °C, held for 2 min, ramped up to 170 °C at a rate of 20 °C min^{-1}, then increased at 15 °C min^{-1} to 260 °C, followed by holding at 260 °C for 6 min, with a total run time of 18.5 min. For *n*-alkanes, initial oven temperature at 50 °C for 2 min, and then increased at 10 °C min^{-1} to 260 °C, with a total run time of 23 min.

The injector, transfer line, quadrupole and source temperatures were set at 280, 250, 150 and 230 °C, respectively. Helium (99.999%) was used as carrier gas at a flow rate of 1.2 mL min^{-1} in spitless mode. The mass spectrometer was operated in the electron ionization (EI) mode using an ionization voltage at 70 eV with a full scan mode at m/z 50-420. To gain the highest possible selectivity and sensitivity, the data acquisition was performed in the selected ion monitoring (SIM) mode and the retention time and selected ions of the analytes was presented in Table S1.

The chemical structure of the PAF-56P material was characterized by a Fourier transform-infrared (FT-IR) spectrum obtained on a Bruker Alpha spectrometer (Ettlingen, Germany) with KBr pellet in the wavenumber range of 500-4000 cm^{-1}. A V-Sorb 2800P surface area and pore size distribution analyzer (Gold APP Instruments, Beijing, China) was used to measure the Brunauer-Emmett-Teller (BET) surface area, N_2 adsorption isotherms and pore sizes. Transmission electron microscopy (TEM) images were recorded on a JEM-2011 HR (JEOL, Japan). The scanning electron microscopy (SEM) images were obtained by a Hitachi S4800 field emission electron microscope (Tokyo, Japan) at an accelerating voltage of 15 kV. The thermal stability of the PAF-6-NPC coating was investigated by a Henven HCT-2 thermogravimetric analyzer (Beijing, China) from room

temperature to 600 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

S2. SPME conditions of *n*-alkanes

The optimum conditions for the DI-SPME of the *n*-alkanes were determined as follows: extraction temperature of 30 °C; extraction time of 40 min; salt addition of 5%, agitation speed of 1000 rpm, desorption temperature of 260 °C, and desorption time of 3 min.

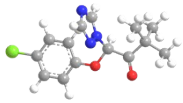
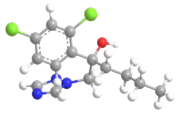
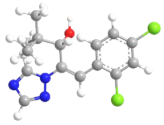
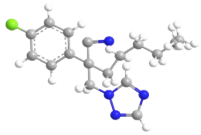
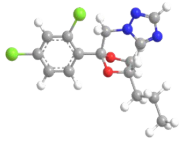
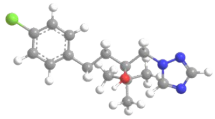
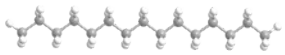
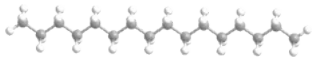
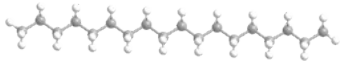
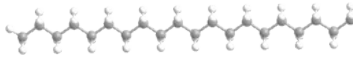
Table S1

Analytical data for the determination of the analytes by the current method.

Analyte	Retention time (min)	Selected ions (m/z)			
Triadimefon	11.357	110	128	181	208
Hexaconazole	12.394	159	175	214	231
Diniconazole	12.584	82	150	179	206
Myclobutanil	13.016	70	165	232	268
Propiconazole	13.546;13.652	69	172	191	259
Tebuconazole	13.871	70	83	125	250

Table S2

Physical-chemical properties of different analytes and the enrichment factors (EFs) for the analytes on the PAF-56P coated fiber.

Compounds	Structure [a]	Molecular weight	logK_{ow} [b]	EFs
Triadimefon		293.7	2.77	154
Hexaconazole		314.2	3.90	255
Diniconazole		326.2	4.30	391
Myclobutanil		288.8	2.94	194
Propiconazole		342.2	3.72	317
Tebuconazole		307.8	3.70	172
n-Pentadecane		212.4	7.71	57
n-Hexadecane		226.4	8.20	75
n-Octadecane		254.5	9.18	87
n-Eicosane		282.5	10.16	90

[a] Red: Oxygen; Blue: Nitrogen; Gray: Carbon; Light gray: Hydrogen; Green: Chlorine.

[b] logK_{ow}: *n*-octanol/water partition coefficients, indicator for hydrophobicity. Data taken from RSC Publishing home: http://www.chemspider.com.

Table S3 Comparison of the current method with some previously reported SPME methods.

Coating	Analytical methods	Real sample	Linear range	LODs	RSDs (%)	Ref.
PDMS-modified	GC-ToFMS	Grapes, Strawberry	5-1000 ng g^{-1}	0.25-5 ng g^{-1}	8.1-16.8	47
PDMS/DVB			5-1000 ng g^{-1}	0.5-5 ng g^{-1}	4.2-12.9	
MIPs	GC-MS	Grape juice	100-2000 ng mL^{-1}	30 ng g^{-1}	5.9-22.1	48
PDMS/DVB	GC-ECD	Juice	0.78-7.80 ng mL^{-1}	0.23-162 ng mL^{-1}	1.2-18.0	49
PDMS/DVB	HPLC-DAD	Fruit	5.5-33.0 ng mL^{-1}	1.5-5.9 ng mL^{-1}	5.4-13.1	50
Modified Nafion/SBA-15	GC-MS	Water	1-2000 ng mL^{-1}	0.01-0.09 ng mL^{-1}	4.3-9.2	51
Poly (VP-co-ED) monolith	HPLC-DAD	Water	0.100-200 ng mL^{-1}	0.014-0.031 ng mL^{-1}	5.6-9.9	52
PAF-56P	GC-MS	Fruits, vegetables	2.50-250 ng g^{-1}	0.15-1.70 ng g^{-1}	3.1-9.2	This study

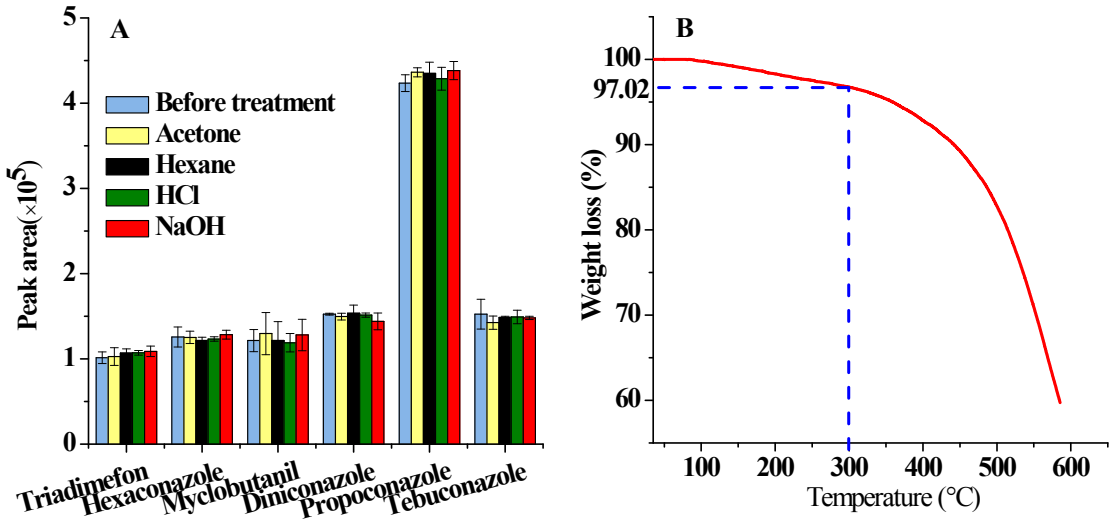


Fig. S1. The chemical stability (A) and thermogravimetric curve (B) of the PAF-56P coating.

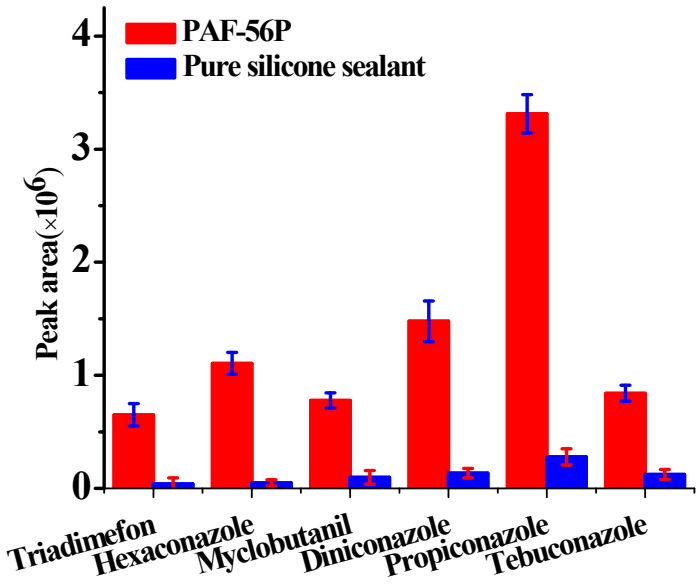


Fig. S2. Comparison of the extraction performance between the PAF-56P coating and the pure silicone sealant coating.