Trace Detection of Organophosphorus Pesticides in Vegetables via Enrichment by Magnetic Zirconia and Temperature-Assisted Ambient Micro-Fabricated Glow Discharge Plasma Desorption Ionization Mass Spectrometry

Yuhan Yang, [ab] Yuting Li, [ab] Zhijun Huang, [ab] Yonghui Tian, [ab] Cheng Qian [c] and Yixiang Duan *[ab]

*Corresponding authors

[a] Research Center of Analytical Instrumentation, Northwest University, Xi'an 710069, Shaanxi, China. E-mail: yduan@nwu.edu.cn

[b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry & Materials Science, Northwest University, Xi'an 710069, Shaanxi, China

[c] Shaanxi Key Laboratory of Earth Surface System and Environmental Carrying Capacity, College of Urban and Environmental Sciences, Northwest University, Xi'an 710127, Shaanxi, China

Table of Contents

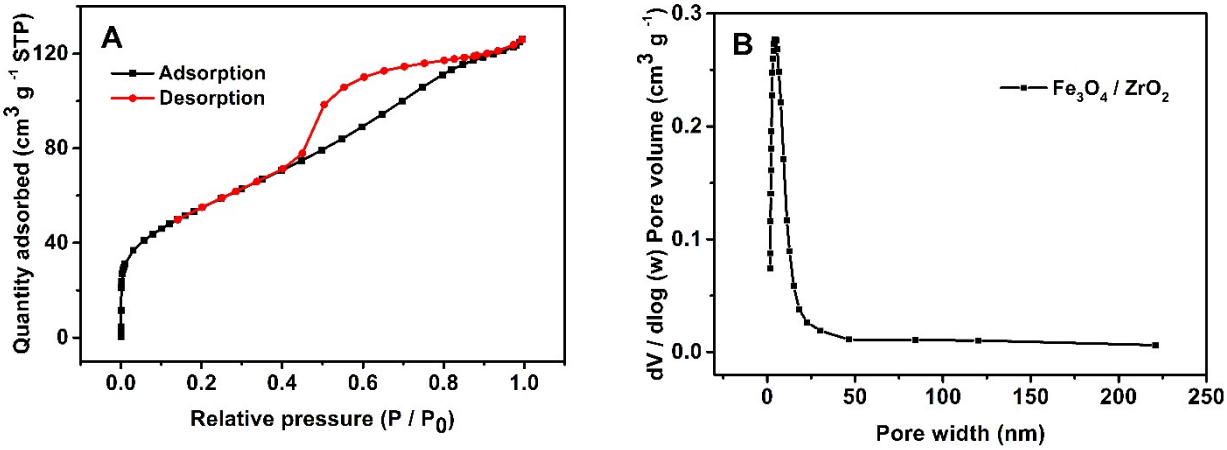


Fig. S1 Characterizations of Fe_3O_4 / ZrO_2 (A) Nitrogen adsorption-desorption isotherms. (B) Pore size distribution curve.

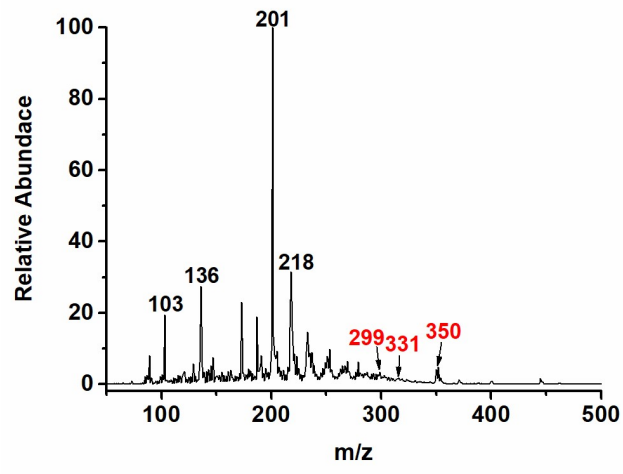
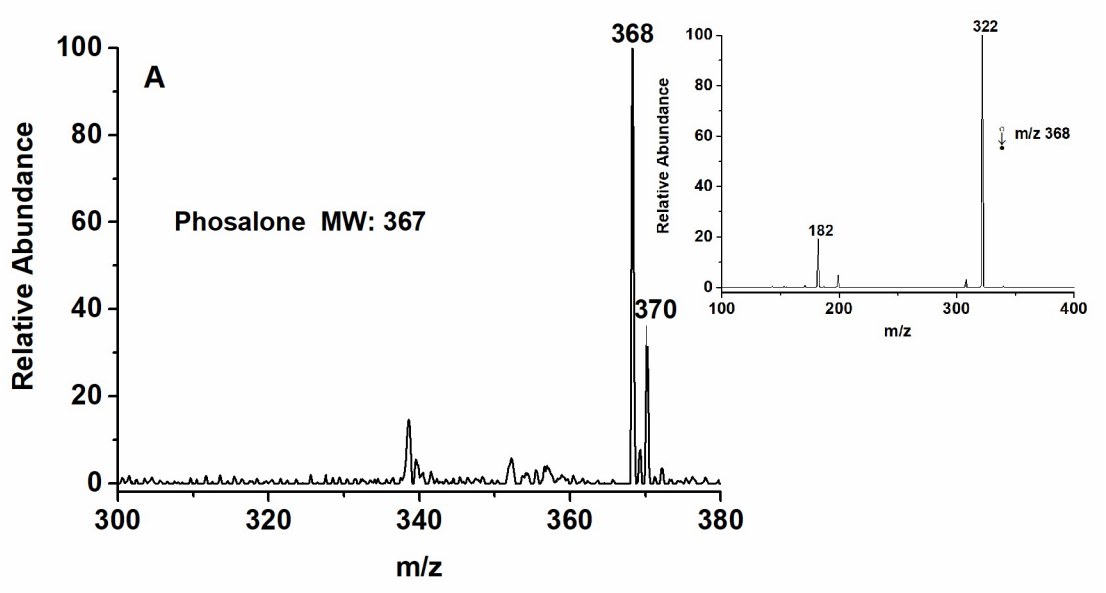
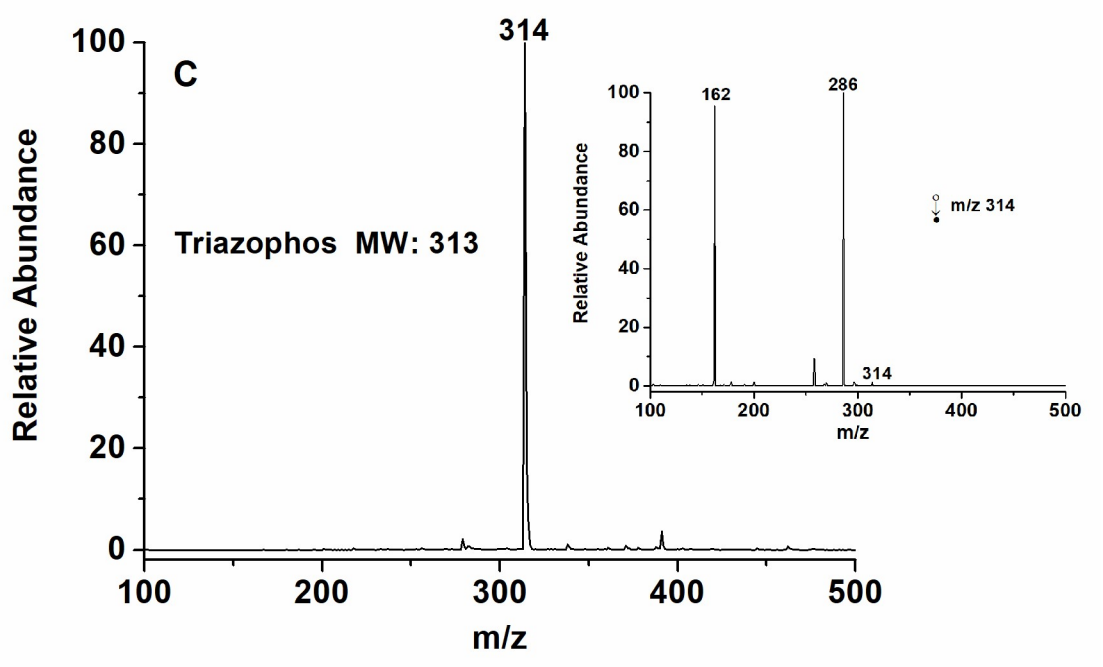
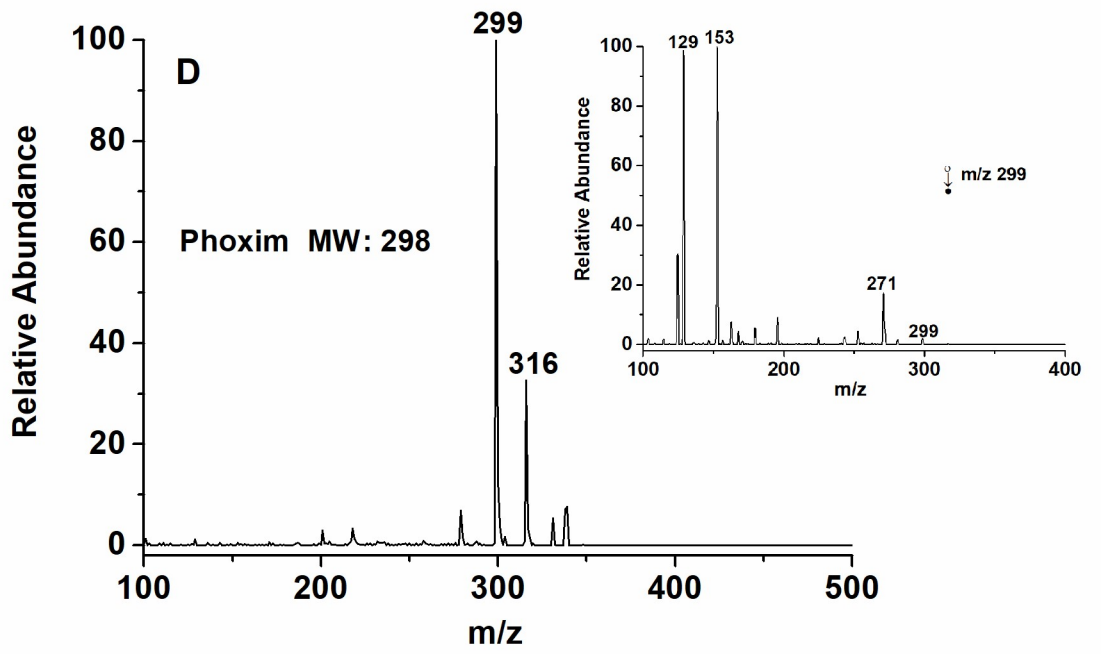
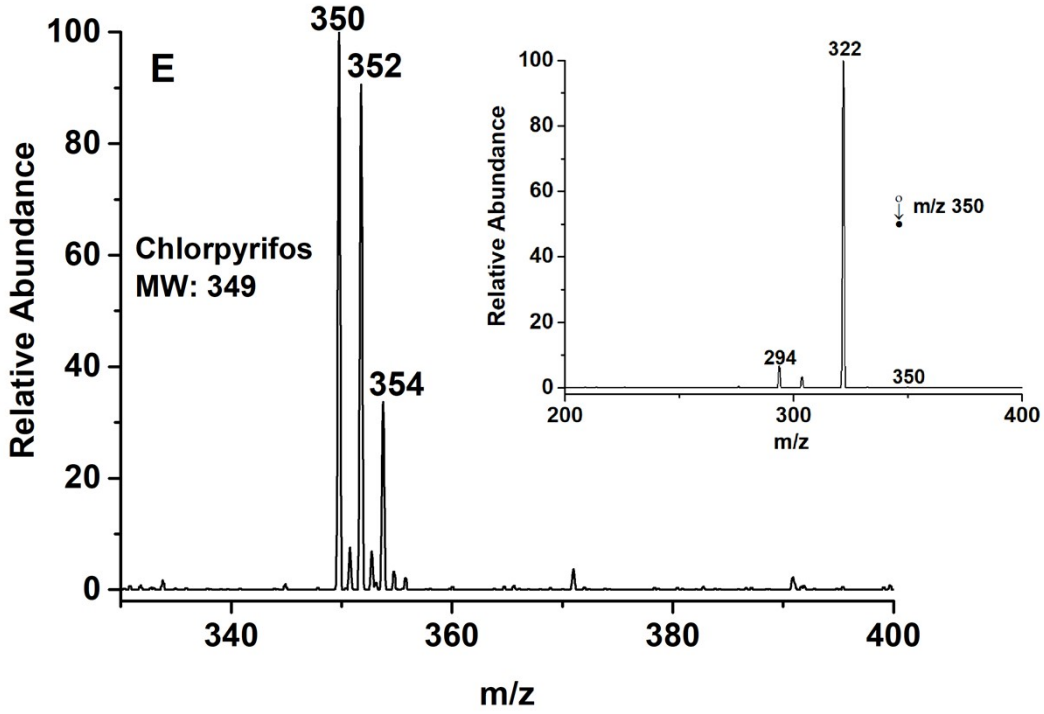


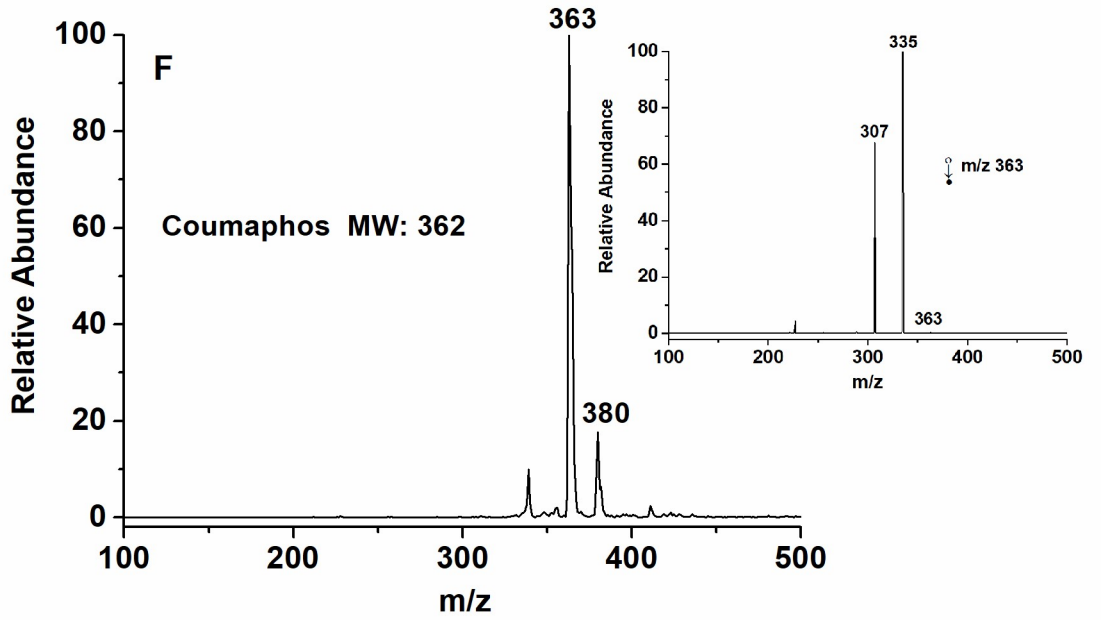
Fig. S2 Mass spectra obtained by MFGDP-MS on a mixed standard solution of 7 OPPs at room temperature. (Phoxim, Malathion and Chlorpyrifos of m/z 299: $[C_{12}H_{15}N_2O_3PS + H]^+$, m/z 331: $[C_{10}H_{19}O_6PS + H]^+$, and m/z 350: $[C_9H_{11}Cl_3NO_3PS + H]^+$; m/z 103: $[2CH_3OH + K]^+$, m/z 136: $[3CH_3OH + K + H]^+$, m/z 201: $[5CH_3OH + Na + NH_4]^+$, m/z 218: $[5CH_3OH + K + Na + H]^+$)


A
Phosalone MW: 367
368
370
Relative Abundance
m/z
322
182
m/z 368
B
Malathion MW: 330
331
348
285
m/z 331


C
Triazophos MW: 313
314
Relative Abundance
m/z
100
80
60
40
20
0
100
200
300
400
500
162
286
m/z 314


D
Phoxim MW: 298
299
316
Relative Abundance
m/z
100
80
60
40
20
0
100
200
300
400
500
129
153
271
299
m/z 299


E
Chlorpyrifos
MW: 349
350
352
354
Relative Abundance
m/z
322
294
350
m/z 350


F
Coumaphos MW: 362
363
380
Relative Abundance
m/z
335
307
363
m/z 363

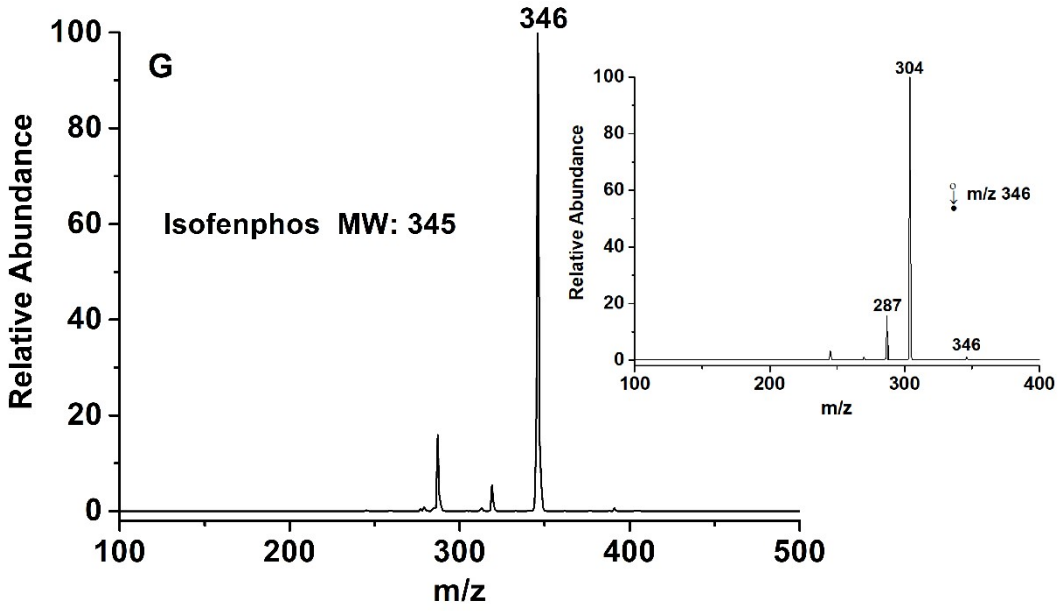


Fig. S3 Mass spectra of protonated (A) Phosalone (m/z 368), (B) Malathion (m/z 331), (C) Triazophos (m/z 314), (D) Phoxim (m/z 299), (E) Chlorpyrifos (m/z 350), (F) Coumaphos (m/z 363), (G) Isofenphos (m/z 346) and insets the CID spectra of 7 kinds of OPPs in the positive mode of He induced Fe_3O_4 / ZrO_2-TCS-MFGDP-MS.

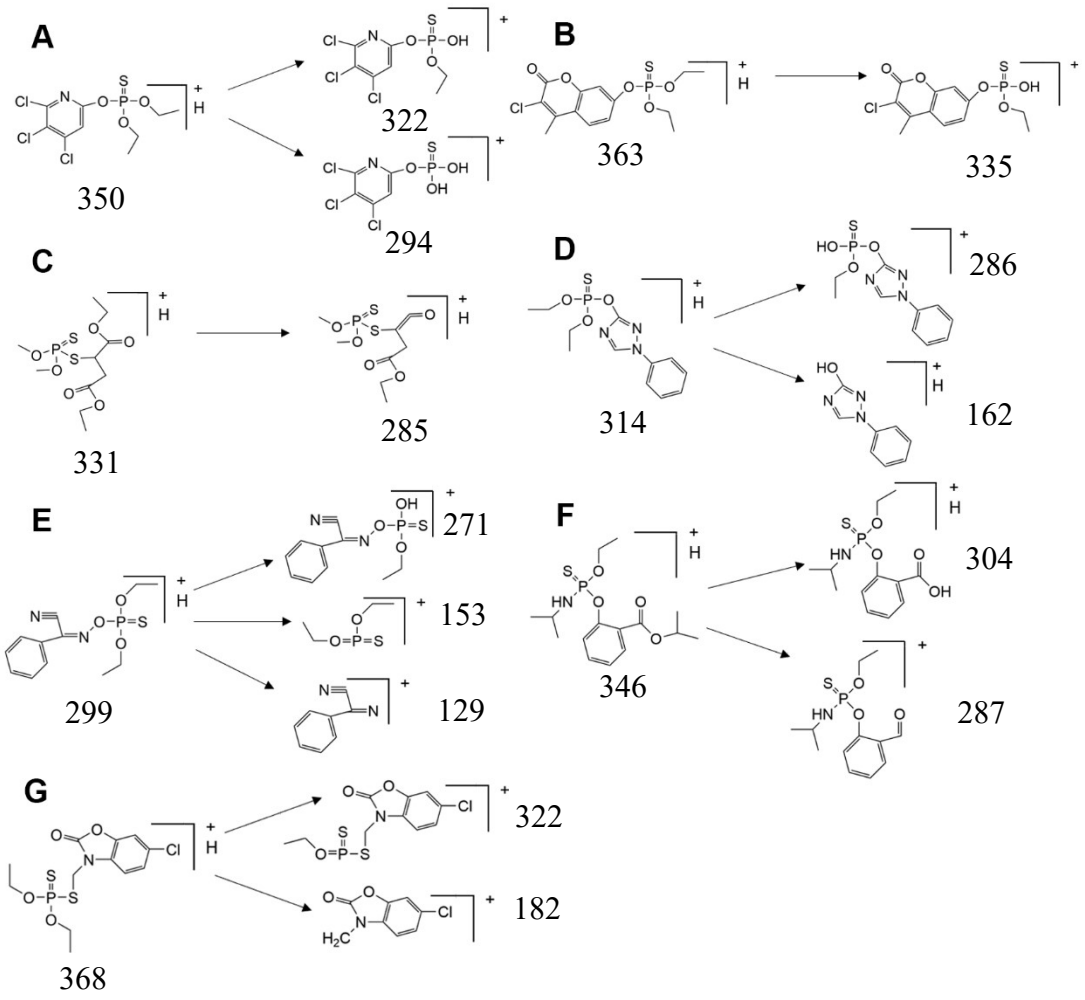


Fig. S4 Possible fragmentation pathways of MFGDP-MS on OPPs: (A) Chlorpyrifos (B) Coumaphos (C) Malathion (D) Triazophos (E) Phoxim (F) Isofenphos (G) Phosalone.

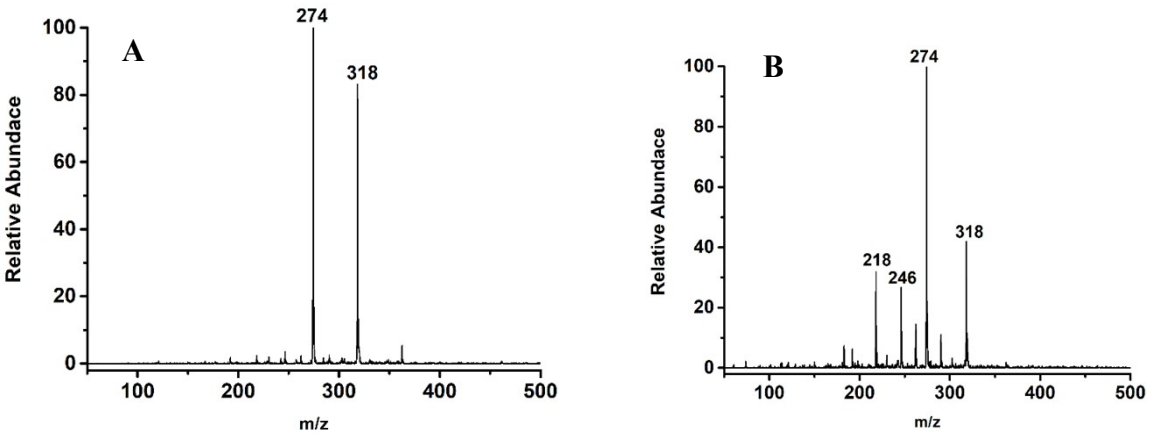


Fig. S5 Mass spectrum after extraction of (A) onion and (B) Chinese cabbage.

The structures of these two ions (m/z 274 and m/z 318) were identified to be N-lauryldiethanolamine and N-(2-hydroxyethyl)-N-(2-(2-hydroxyethoxy) ethyl) dodecylamine. These interferences were found to be leached from the plastic microcentrifuge tubes used during sample pretreatment. The N-lauryldiethanolamine and other ethoxylated aliphatic alkylamines are common plastic antistatic agents.

Table S1 The retention time of $[M + H]^+$ characteristic ions of 7 OPPs

Analytes	**The retention time of ions (min)**
Chlorpyrifos	0.11
Coumaphos	0.30
Malathion	0.20
Triazophos	0.29
Phoxim	0.18
Isofenphos	0.19
Phosalone	0.28

UPLC-MS Detection of OPPs

Sample preparation

10.0 g of the homogeneous sample was put into a 50.0 mL centrifuge tube, after adding 10.0 mL of acetonitrile, the tube was shaken for 1 min. Secondly, after adding 1.0 g NaCl and 4.0 g anhydrous $MgSO_4$, the tube was vortexed again for 1 min and centrifuged for 5 min at 5000 rpm. Then, 1mL of supernatant was transferred to a centrifuge tube containing 250 mg PSA and 150 mg $MgSO_4$, and vortexed for 1min. The mixture was centrifuged at the rate of 6000 rpm for 1 min. Finally, the supernatant was passed through an organic filter membrane for UPLC-MS analysis.

UPLC-MS analysis

Q-FT-Orbitrap-UPLC-MS equipped with ESI source (Thermo Fisher Scientific) was used.

Parameters of UPLC: Chromatographic separation was accomplished using a 50 mm long by 2.1 mm i.d. microcolumn packed with 1.9 μm Thermo Hypersil GOLD C18 stationary phase. The mobile phase of UPLC consisted of 0.1 % formic acid in water (A) and methanol (B) at a flow rate of 300 μL min^{-1}. Linear gradient condition was as follows:(1) 0.00-2.00 min, 95.0-95.0 % A, (2) 2.00-6.00 min, 95.0-10.0 % A, (3) 6.00-8.00 min, 10.0-10.0 % A, (4) 8.00-8.10 min, 10.0-95.0 % A, (5) 8.10-12.00 min, 95.0-95.0 % A. The column heater was set to 30 ℃ and injection volume was set to 2 μL.

Parameters of MS analysis: Full MS mode with positive electrospray ionization (ESI+) was performed for the detection of OPPs. Spray voltage was 3.5 kV. Aux gas was N_2 with the temperature of 320 ℃.

Table S2 Recoveries obtained by UPLC-MS analysis of 7 kinds of OPPs

Analytes	Spiked (μg kg $^{-1}$)	Onions		Spiked (μg kg $^{-1}$)	Chinese cabbages	
		Recovery (%, n=3)	RSD (%, n=3)		Recovery (%, n=3)	RSD (%, n=3)
Chlorpyrifos	50	94.6	4.8	50	85.4	1.1
	100	82.0	2.5	100	86.2	2.8
	150	82.2	12.9	500	90.1	9.1
Coumaphos	50	84.7	1.3	50	91.4	0.2
	100	82.1	0.5	100	98.7	0.3
	150	89.6	4.2	500	92.8	0.8
Malathion	50	94.8	3.6	50	94.9	0.8
	100	79.0	1.9	100	105.3	0.4
	150	74.1	0.6	500	89.8	0.1
Triazophos	50	90.7	4.2	50	88.0	0.7
	100	78.7	0.2	100	91.8	0.6
	150	97.2	3.2	500	113.9	2.9
Phoxim	50	88.9	4.9	50	102.4	0.6
	100	82.6	0.7	100	94.9	0.3
	150	71.2	5.8	500	84.0	2.4
Isofenphos	50	97.4	10.8	50	114.0	1.3
	100	77.3	2.2	100	105.0	5.1
	150	101.5	7.8	500	89.0	4.6
Phosalone	50	70.7	0.5	50	88.2	0.6
	100	90.4	0.2	100	87.7	0.9
	150	97.6	0.1	500	97.8	1.8