Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary material

Manuscript Title: Analysis of low volatility pesticides in cabbage by high temperature comprehensive two-dimensional gas chromatography

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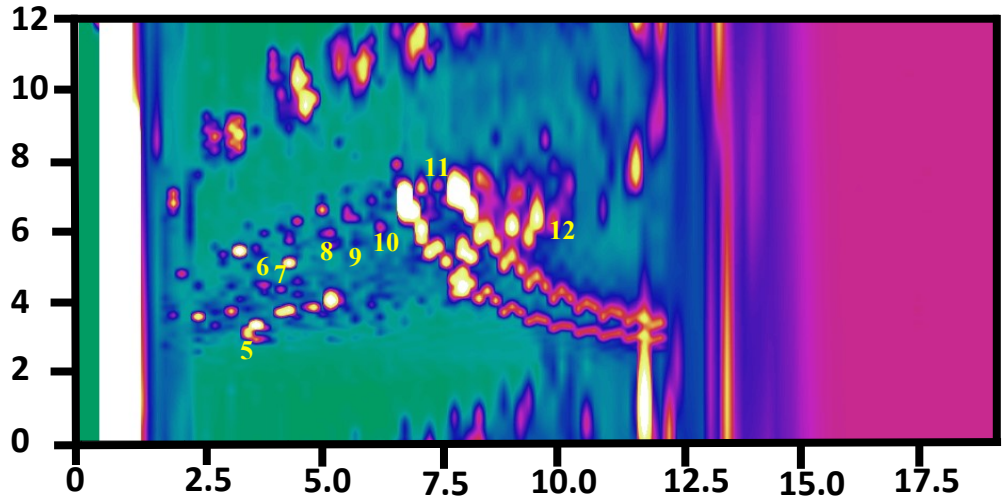

Fig. S1. The contour plots obtained from analysis of the 8 pesticides (**5-12**) spiked into the cabbage samples with the final concentration of 5 mg/kg using the selected HTGC×GC method: the constant trap temperature of 10 °C, initial oven temperature of 80 °C, ramp rate of 15 °C/min and P_M of 12 s.

Spiked sample at low concentration (10 times)

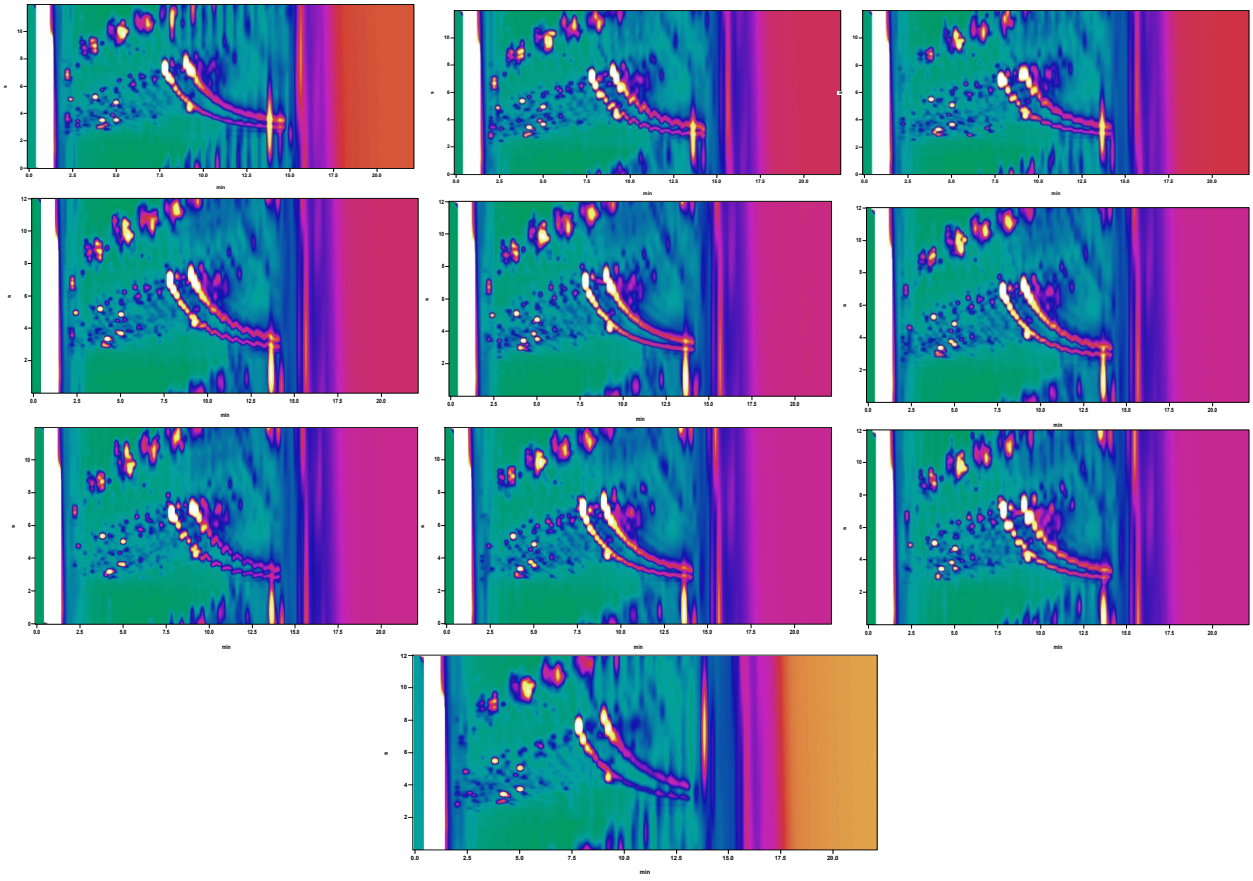

Fig. S2. The contour plots obtained from 10 repeated analyses of the 8 pesticides (**5-12**) spiked into the cabbage samples with the final concentration of 0.5 mg/kg using the selected HTGC×GC method.

Table S1. Validation of the HTGC×GC-FID for the 8 pesticides.

Peak No.	Compound	LOD (ppm)	Calibration curve	Recovery (%) (at 0.5 mg/kg) (*n* = 3)	S/N at 0.1 ppm	Precision	
						Intra day	Inter day
5	Metolcarb	0.0385	y = 13.487x + 0.2578 (R^2 = 0.9848)	93.61±6.37	4.26	7.39	10.20
6	Isoprocarb	0.0910	y = 5.4895x + 0.1849 (R^2 = 0.9985)	97.95±0.31	8.52	6.64	5.14
7	Methiocarb	0.0878	y = 2.918x + 0.9949 (R^2 = 0.9947)	88.29±0.30	16.7	4.45	2.52
8	Carbofuran	0.0098	y = 10.567x + 1.2333 (R^2 = 0.9878)	102.62±1.85	18.2	5.28	2.30
9	Heptachlor	0.0179	y = 6.7585x + 0.2105 (R^2 = 0.9926)	97.35±0.26	15.7	1.89	8.16
10	Chlorpyrifos	0.0239	y = 14.523x + 0.1275 (R^2 = 0.9909)	90.72±1.77	26.9	3.47	2.57
11	Dicofol	0.0138	y = 21.769x + 1.2632 (R^2 = 0.9891)	96.11±0.21	25.1	9.80	3.71
12	Permethrin	0.0139	y = 12.465x + 0.3671 (R^2 = 0.9728)	95.71±0.67	29.1	6.03	3.43

Table S2. Method detection limit (mg/kg) of the twelve pesticides between experiment and literature.

No.	Name	Method detection limit (mg/kg)	
		This work	MRL*
1	4,4'-DDT	0.01	0.2 (carrot)[a]
2	β-endosulfan	0.01	1 (cucumber)[b]
3	Endosulfan sulfate	0.02	1 (cucumber)[b]
4	Endrin	0.04	0.05 (fruiting vegetables, cucurbits)
5	Metolcarb	0.04	No data
6	Isoprocarb	0.09	No data
7	Methiocarb	0.09	0.1 (cabbages, head)
8	Carbofuran	0.01	0.01 (banana)
9	Heptachlor	0.02	0.02 (cereal grains)
10	Chlorpyrifos	0.02	1 (cabbages, head)
11	Dicofol	0.01	0.1 (Spices, fruits and berries)
12	Permethrin	0.01	5 (cabbages, head)

***** Reference from http://www.fao.org/fao-who-codexalimentarius/about-codex/en/

[a] Sum of p,p'-DDT, o,p'-DDT, p,p'-DDE and p,p'-TDE (DDD)

[b] Sum of α-endosulfan, β-endosulfan and endosulfate sulfate

Table S3. The average chromatographic parameters; peak times and peak width in ^{1}D and ^{2}D separations (^1t_R (min), ^2t_R (s), ^1W (min) and ^2W (s)) of each target pesticide (n=5) with the concentration of 0.5 mg/L using the initial oven temperature of 80°C and temperature ramp rate of 15°C/min. The relative standard deviations of ^1t_R, ^2t_R, ^1W and ^2W were within the ranges of 0.0006 - 0.0045 %, 0.0330 - 0.2700 %, 0.0024 - 0.0150 % and 0.0004 - 0.0033 %, respectively.

Compound	Average parameter			
	^1t_R	^2t_R	^1W	^2W
4,4'-DDT	9.67	4.43	0.05	0.01
Endrin	10.69	5.15	0.03	0.01
β-endosulfan	10.49	5.56	0.05	0.01
Endosulfan sulfate	7.66	3.88	0.03	0.02

Table S4. The average ^2W at different LMCS trapping temperature programs; constant trap and stepped temperature, of the standard mixture (100 mg/L each) and extracted cabbage sample using the initial oven temperature of 80°C, temperature ramp rate of 15°C/min and modulation period (P_M) of 12 s.

Condition	Average ^2W (min)	
	Standard mixture	Extracted cabbage
Constant trap temperature of 10 °C	0.015	0.020
Stepped trap temperature	0.027	0.026

Table S5. The average peak height at different initial oven temperatures of the standard mixture (100 mg/L each) and the extracted cabbage sample using temperature ramp rate of 15 °C/min, modulation period (P_M) of 12 s and constant trap temperature of 10 °C for ^2W experiment, respectively.

Initial oven temperature (°C)	Average peak height (pA)	
	Standard mixture	Extracted cabbage
40	38.7	21.9
80	87.8	22.7
120	42.8	29.3

Table S6. The average peak height at different temperature ramp rate of the standard mixture (100 mg/L each) and extracted cabbage sample using initial oven temperature of 80 °C, modulation period (P_M) of 12 s and constant trap temperature of 10 °C for ^2W experiment, respectively.

Temperature ramp rate (°C/min)	Average peak height (pA)	
	Standard mixture	Extracted cabbage
4	16.9	11.3
8	51.0	12.2
15	87.8	22.7

Table S7. The approximated ^1W, average ^2W and average peak heights at different P_M of the standard mixture (100 mg/L each) and extracted cabbage sample using initial oven temperature of 80 °C, temperature ramp rate of 15 °C/min and constant trap temperature of 10 °C.

P_M (s)	Approximated ^1W (min)	Average ^2W (min)		Average peak height (pA)	
		Standard mixture	Extracted cabbage	Standard mixture	Extracted cabbage
8	0.133	0.015	0.023	73.4	21.0
12	0.200	0.015	0.025	87.8	51.7