Application Note

Food Testing and Agriculture

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Analysis of Organophosphorus and Organochlorine Pesticides in Fruit and Vegetables Using an Agilent 8890 GC with Four Detectors

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Abstract

This Application Note describes an effective and reliable analytical method for the determination of organophosphorus and organochlorine pesticide residues in fruit and vegetables following the China Standard NY/T 761-2008.[1] An unpurged two-way capillary flow technology (CFT) device was used to split the sample 1:1 onto two columns then to two detectors. Compared with the traditional pretreatment procedure described in NY/T 761-2008, a simplified Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method was used in this application, and provided sufficient sample matrix cleanup while preserving low-level analyte detection. Area repeatability, linearity, and recovery were evaluated for both organophosphorus and organochlorine pesticides using an Agilent 8890 GC system with four detectors.

Introduction

The use of pesticides has played an important role in the prevention and control of pests and the resulting improvement of agricultural yields. Two common pesticide classes used in agricultural treatments have organophosphorus and organochlorine chemical structures.

For the determination of organophosphorus and organochlorine pesticide residues in fruit and vegetables, gas chromatography (GC), gas chromatography/mass spectrometry (GC/MSD), and gas chromatography/tandem mass spectrometry (GC/QQQ) methods are widely used. Correspondingly, China has issued a series of standards for the determination of those pesticides. NY/T 761-2008 describes a GC method with an electron capture detector (ECD) and flame photometric detector (FPD). GB/T 19648-2006[2] describes a GC/MSD method for 500 pesticides, and GB 23200.113-2018[3] is a GC/QQQ method for 208 pesticides. Mass spectrometry methods have obvious advantages in qualitative analysis, and can determine dozens or even hundreds of pesticide residues simultaneously with high efficiency. Consequently, the price of the instrument is relatively expensive. Although gas chromatography has less qualitative ability than MS, it is still welcomed by many labs because of its selective detectors and low detection cost. ECD has excellent selectivity for chlorine, and is a good choice for the analysis of organochlorine pesticides. FPD has high selectivity for sulfur and phosphorus, and it is a good choice for the analysis of organophosphorus pesticides. In the NY/T 761 method, a primary column and confirmation column are used in tandem to achieve accurate qualitative analysis and prevent false-positive results. This dual-column approach also provides quantitative results for both organophosphorus and organochlorine pesticides when used with two FPDs and two ECDs. Normally, labs need two GC systems to follow the NY/T 761 method strictly. However, the 8890 GC can have two FPDs and two ECDs installed on one instrument to provide greater flexibility compared to other lab GCs. For both organophosphorus and organochlorine pesticides analysis, labs do not need to change hardware; the only thing they need to do is to reinstall different columns onto different detectors.

Sample pretreatment is important for the analysis of multipesticide residues, which directly affects the work efficiency and sensitivity. The NY/T 761 method uses traditional, labor-intensive extraction and cleanup procedures for sample pretreatment. The cleanup procedure of organochlorine pesticides and organophosphorus pesticides is different. That means two different pretreatments are needed for the same sample when organophosphorus and organochlorine pesticides both need to be tested. The popular sample pretreatment method of QuEChERS is the optimal method for high-throughput sample analysis. Most importantly, the same sample pretreatment process can be used both for organophosphorus and organochlorine pesticides, which greatly improves the analysis efficiency.

Experimental

Instrumentation

An 8890 GC with an SSL inlet equipped with two ECDs and two FPDs was used for this series of experiments. An unpurged two-way CFT device was used to split the sample 1:1 onto two columns for detection on two detectors. For organophosphorus pesticides analysis, the primary column and confirmation column were Agilent HP-50+ and Agilent HP-1. A dual-column, dual-ECD system with an Agilent DB-5 primary analysis column and an Agilent DB-17 confirmatory column was used to separate the organochlorine pesticides. The analysis on organophosphorus pesticides and organochlorine pesticides analysis cannot be run simultaneously because of their different temperature programs. Compared with the Agilent 7890 GC, which can only install three detectors at most, the 8890 GC is more flexible, and can install four detectors at the same time. Therefore, labs do not need to change the hardware; they must only reinstall the appropriate columns to the right detectors. Figure 1 shows the schematics for the instrument setup. Table 1 lists the chromatographic conditions used for these analyses.

Reagents and chemicals

All reagents and solvents were HPLC grade. Acetonitrile (ACN) and hexane were purchased from J&K Scientific LTD. Acetone was purchased from ANPEL Laboratory Technologies (Shanghai) Inc. All organophosphorus and organochlorine single standards were purchased from J&K Scientific LTD and ANPEL Laboratory Technologies (Shanghai) Inc.

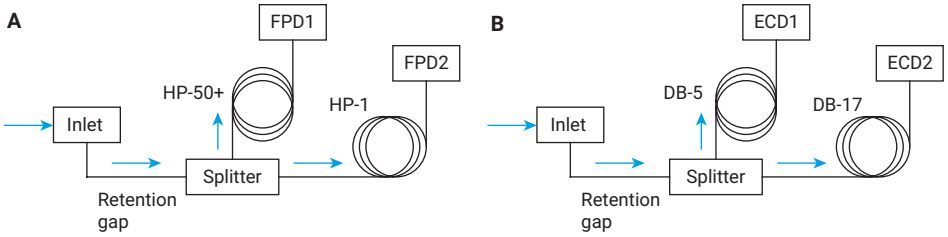


Figure 1. Agilent capillary flow technology two-way splitter without makeup gas (p/n G3181B) and diagram of instrument setup of simultaneous confirmation from a single injection onto both the primary and confirmation columns. (A) FPDs for phosphorus detection, (B) ECDs for chlorine detection.

Table 1. Chromatographic conditions.

Organophosphorus method	
GC	**Agilent 8890 GC equipped with two FPDs**
Inlet	Split/splitless Temperature: 220 °C Splitless mode, purge flow 60 mL/min at 0.75 min.
Liner	Agilent Ultra Inert, splitless, single taper, glass wool (p/n 5190-2293)
Injection	2 µL
Retention Gap	0.5 m × 0.53 mm id deactivated fused silica tubing (p/n 160-2535-5)
Column	Column1: Agilent HP-50+ 30 m × 0.53 mm, 1 µm (p/n 19095L-023) Column2: Agilent HP-1 30 m × 0.53 mm, 1.5 µm (p/n 19095Z-323)
Carrier	Nitrogen, 10 mL/min, constant flow (the column flow is the same for column 1 and 2)
Oven	150 °C (2 minutes), 8 °C/min to 250 °C (12 minutes)
FPD Plus 1 and 2	Temperature: 250 °C Emission block: 150 °C Hydrogen: 60 mL/min Air: 60 mL/min Make-up gas (N_2): 60 mL/min

Organochlorine method	
GC	**Agilent 8890 GC equipped with two ECDs**
Inlet	Split/splitless Temperature: 200 °C Split mode, split ratio: 10:1
Liner	Agilent Ultra Inert, split, low pressure drop, glass wool (p/n 5190-2295)
Injection	2 µL
Retention Gap	0.5 m × 0.53 mm id deactivated fused silica tubing (p/n 160-2535-5)
Column	Column1: Agilent DB-5 30 m × 0.25 mm, 0.25 µm (p/n 122-5032) Column2: Agilent DB-17 30 m × 0.25 mm, 0.25 µm (p/n 122-1732)
Carrier	Nitrogen, 1 mL/min, constant flow (the column flow is the same for column 1 and 2)
Oven	150 °C (2 minutes), 6 °C/min to 270 °C (12 minutes, hold 23 minutes for deltamethrin analysis)
ECD 1 and 2	Temperature: 320 °C Make-up gas (N_2): 25 mL/min

Solutions and standards

Table 2 shows 54 organophosphorus pesticides divided into four groups. According to the response values of each pesticide on the instrument, a certain volume of single pesticide standard solution of the same group was accurately added and diluted with acetone. The same method was used to prepare four groups of stock solutions of organophosphorus pesticide mixture. Calibration standards were diluted by matrix blank (see Sample preparation).

Table 2. Data results for organophosphorus pesticides analysis on an Agilent HP-50+ column.

No.	Name	Linearity Range (mg/kg)	R^2	% RSD (n = 8)			MDL (mg/kg)	% Recovery	Group
				Low	Middle	High			
1	Dichlorvos	0.05–0.5	0.9982	2.8	1.5	1.5	0.004	108.9	1
2	Acephate	0.05–0.5	0.9989	4.6	3.1	1.6	0.007	97.7	1
3	Dicrotophos	0.05–0.5	0.997	4.3	2.3	1.6	0.007	105.3	1
4	Disulfoton	0.05–0.5	0.9984	3.1	2.7	2.1	0.006	118.2	1
5	Dimethoate	0.05–0.5	0.9981	0.6	1.6	1.3	0.002	111.4	1
6	Parathion-methyl	0.05–0.5	0.9984	1.6	2.1	1.6	0.003	116	1
7	Chlorpyrifos	0.05–0.5	0.9982	2.7	1.7	1.3	0.003	115.1	1
8	Pirimiphos-ethyl	0.05–0.5	0.9985	2.6	1.4	1.4	0.003	111.8	1
9	Fenthion	0.05–0.5	0.999	3	2.4	1.6	0.005	111	1
10	Phoxim	0.2–2.0	0.9922	4.4	2.8	3.6	0.05	110.9	1
11	Ditalimfos	0.05–0.5	0.9994	2.6	1.6	1.1	0.004	70.4	1
12	Triazophos	0.05–0.5	0.9992	3.6	2	2.4	0.007	104.5	1
13	Phosmet	0.2–2.0	0.9998	2.2	2.2	1.6	0.009	102	1
14	Trichlorfon	0.2–2.0	0.999	3	3.5	2.2	0.05	115.4	2
15	Ethoprophos	0.05–0.5	0.9987	1.2	1.5	1.9	0.004	98.5	2
16	Phorate	0.05–0.5	0.9988	2	1.2	1.9	0.004	97.4	2
17	Omethoate	0.05–0.5	0.9982	4.5	3.7	1.8	0.008	102.5	2
18	Diazinon	0.05–0.5	0.998	2.5	1.5	1.9	0.006	95	2
19	Fonofos	0.05–0.5	0.9968	3.5	2.3	2.2	0.003	87.4	2
20	Chlorpyrifos-methyl	0.05–0.5	0.9986	2.4	1.2	1.7	0.004	92.1	2
21	Paraoxon	0.05–0.5	0.9991	3.5	2	1.1	0.007	97.2	2
22	Fenitrothion	0.05–0.5	0.9992	2.9	2.8	1.4	0.005	97.4	2
23	Bromophos	0.05–0.5	0.9986	3.6	3.1	1.1	0.009	100.2	2
24	Bromophos-ethyl	0.05–0.5	0.999	2.2	1.6	0.9	0.007	101	2
25	Profenofos	0.05–0.5	0.9995	3.4	2.7	0.8	0.008	104.7	2
26	Ethion	0.05–0.5	0.9995	1.6	1.7	0.8	0.004	111.6	2
27	Pyrazophos	0.2–2.0	0.9998	2.4	3.1	2.4	0.02	108.6	2
28	Coumaphos	0.2–2.0	0.9997	4.2	2.6	2.6	0.02	107.1	2
29	Methamidophos	0.05–0.5	0.9999	3.5	3.2	2.9	0.004	107.7	3
30	Sulfotep	0.05–0.5	0.9999	2.1	1.2	1.7	0.001	94.1	3
31	Terbufos	0.05–0.5	0.9999	2.2	2.1	2.2	0.003	94	3
32	Monocrotophos	0.05–0.5	0.9995	3.2	0.8	1.6	0.004	93.4	3
33	Dichlofenthion	0.05–0.5	0.9999	3.4	1.7	1.4	0.003	93.2	3
34	Fenchlorphos	0.05–0.5	0.9999	2.2	1.4	1.5	0.003	94.7	3
35	Pirimiphos-methyl	0.05–0.5	0.9999	2.8	2	1.5	0.004	94.2	3
36	Parathion	0.05–0.5	0.9997	3.2	1.5	1.3	0.003	93.9	3
37	Isofenphos	0.05–0.5	0.9999	3.9	3	2.1	0.005	93.5	3
38	Methidathion	0.05–0.5	0.9998	2.7	1.7	1.3	0.004	93.6	3
39	Phosfolan-methyl	0.05–0.5	0.998	2.3	2.9	1.7	0.01	102	3
40	Famphur	0.05–0.5	0.9999	2.7	2.6	3.2	0.02	102	3
41	Phosalone	0.2–2.0	0.9993	2.9	3.1	2.3	0.008	102	3
42	Azinphos-ethyl	0.2–2.0	0.9996	2.8	2.3	1.7	0.02	116.5	3
43	Naled	0.1–1.0	0.9999	2.6	3.3	1.9	0.02	95.5	4
44	Mevinphos	0.05–0.5	0.9998	3.9	2.6	1.3	0.005	118.1	4
45	Propetamphos	0.05–0.5	0.9995	4	2.8	1.4	0.007	101.5	4

Table 3 shows 41 organochlorine pesticides divided into three groups. A certain volume of single pesticide standard solution of the same group was accurately added and diluted with hexane. The same method was used to prepare three groups of stock solutions of organochlorine pesticide mixture. Calibration standards were diluted by matrix blank (see Sample preparation).

Table 2. Data results for organophosphorus pesticides analysis on an Agilent HP-50+ column (continued).

No.	Name	Linearity Range (mg/kg)	R^2	% RSD (n = 8)			MDL (mg/kg)	% Recovery	Group
				Low	Middle	High			
46-1	Phosphamidon-1	0.1–1.0	0.9999	3.6	1.9	0.9	0.02	100.7	4
46-2	Phosphamidon-2								4
47	Trichloronate	0.05–0.5	0.9999	2.3	2.7	1.1	0.004	97.5	4
48	Malathion	0.05–0.5	0.9999	1.9	1.9	1	0.005	98.1	4
49	Isocarbophos	0.05–0.5	0.9999	2.6	1.8	1	0.004	96.9	4
50	Quinalphos	0.05–0.5	0.9999	2.8	1.6	1	0.004	97	4
51	Tetrachlorvinphos	0.05–0.5	0.9998	2.1	2.4	0.8	0.007	97.9	4
52	Phosfolan	0.05–0.5	0.9999	2.7	3.3	2.5	0.02	97.2	4
53	EPN	0.05–0.5	0.9993	2.8	3.8	1.8	0.009	100.4	4
54	Azinphos-methyl	0.2–2.0	0.9995	2	3.7	1.5	0.02	91.3	4

Table 3. Data results for organochlorine pesticides analysis on an Agilent DB-5 column.

No.	Name	Linearity Range (mg/kg)	R^2	% RSD (n = 8)			MDL (mg/kg)	% Recovery	Group
				0.05 mg/kg	0.1 mg/kg	0.5 mg/kg			
1	α-BHC	0.05–0.5	0.9996	1.1	1.2	1	0.00003	98.6	1
2	Simazine	0.05–0.5	0.9931	0.8	1.3	1	0.002	88.1	1
3	Atrazine	0.05–0.5	0.9912	2.1	0.9	1	0.002	78.3	1
4	δ-BHC	0.05–0.5	0.9991	0.6	1.3	1	0.00003	93.7	1
5	Heptachlor	0.05–0.5	0.9996	0.8	1.1	0.8	0.00003	118.6	1
6	Aldrin	0.05–0.5	0.9997	0.6	1.2	0.8	0.00004	108.5	1
7	*o,p'*-DDE	0.05–0.5	0.9997	1.1	1.2	0.7	0.00004	101.7	1
8	*p,p'*-DDE	0.05–0.5	0.9998	0.7	1.1	0.9	0.00005	106.6	1
9	*o,p'*-DDD	0.05–0.5	0.9996	1.2	1.1	0.8	0.00004	77.3	1
10	*p,p'*-DDT	0.05–0.5	0.9997	0.9	0.5	0.5	0.00006	111	1
11	Iprodione	0.05–0.5	0.9974	1	1.3	1.7	0.0007	113.5	1
12	Bifenthrin	0.05–0.5	0.9998	1	1.7	0.8	0.0002	116	1
13	*cis*-Permethrin	0.05–0.5	0.9999	1.6	2.2	0.8	0.0004	114	1
14-1	Cyfluthrin-1	0.05–0.5	0.9982	2.8	1.8	1.1	0.0005	114.8	1
14-2	Cyfluthrin-2								1
14-3	Cyfluthrin-3								1
14-4	Cyfluthrin-4								1
15-1	*tau*-Fluvalinate-1	0.05–0.5	0.999	2.8	1.4	0.7	0.0005	105	1
15-2	*tau*-Fluvalinate-2								1
16	β-BHC	0.05–0.5	0.9998	1	0.2	0.8	0.00007	89.2	2
17	γ-BHC	0.05–0.5	0.9999	1.4	0.3	0.9	0.00003	94.7	2
18	Pentachloronitrobenzene	0.05–0.5	0.9999	1.2	0.2	0.9	0.00003	91.6	2
19	Propanil	0.05–0.5	0.9999	4	1.1	1	0.0002	98.7	2
20	Vinclozolin	0.05–0.5	0.9999	1.9	1.3	0.8	0.00009	89.4	2
21-1	Endosulfan-1	0.05–0.5	0.9984	2.1	0.5	0.8	0.00008	94.8	2
21-2	Endosulfan-2								2
22	*p,p'*- DDD	0.05–0.5	0.9995	3.8	2	1	0.00006	96.4	2
23	Dicofol	0.05–0.5	0.9982	2	2.8	3.3	0.0006	95.6	2
24	*Lambda*-cyhalothrin	0.05–0.5	0.9991	2.1	0.4	0.9	0.0001	94.1	2
25	Permethrin	0.05–0.5	0.9987	2.3	1.3	2.2	0.0005	107.5	2

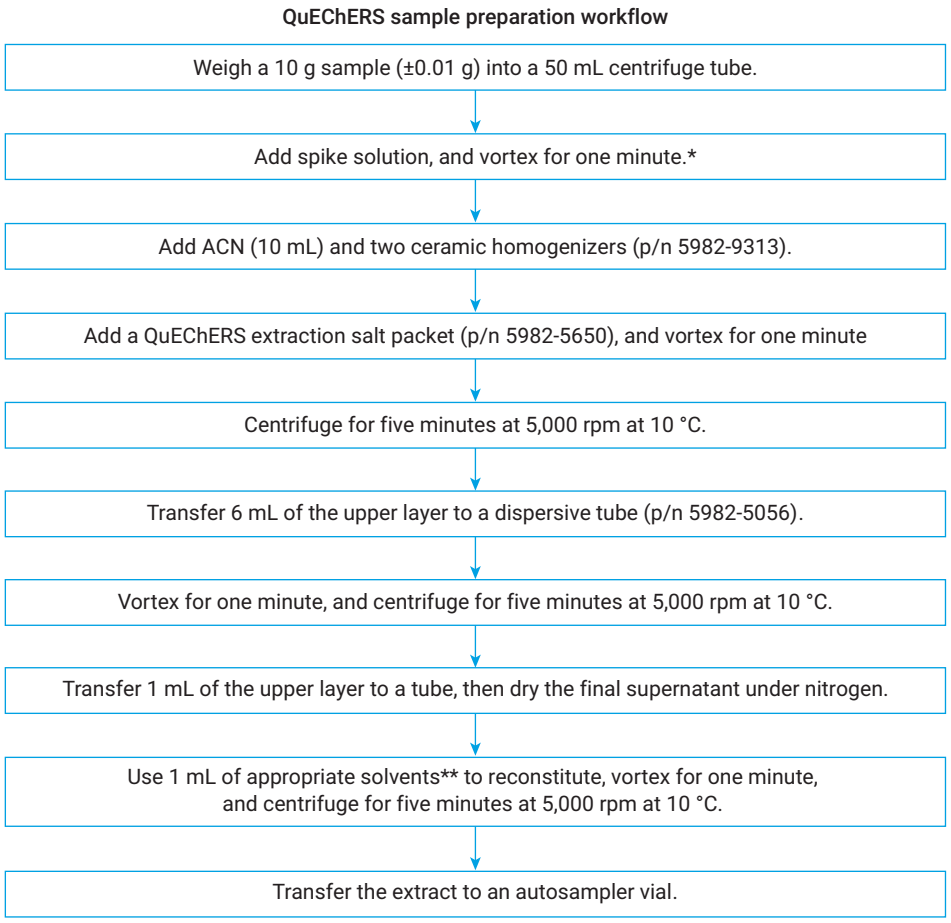
Table 3. Data results for organochlorine pesticides analysis on an Agilent DB-5 column (continued).

No.	Name	Linearity Range (mg/kg)	R^2	% RSD (n = 8)			MDL (mg/kg)	% Recovery	Group
				0.05 mg/kg	0.1 mg/kg	0.5 mg/kg			
26-1	Flucythrinate-1	0.05–0.5	0.991	1.3	0.4	1	0.0005	92	2
26-2	Flucythrinate-2								2
27	Dicloran	0.05–0.5	0.9998	1.2	1.7	1.7	0.00006	80.1	3
28	Hexachlorobenzene	0.05–0.5	0.9997	0.9	1.8	0.5	0.00004	85.2	3
29	Chlorothalonil	0.05–0.5	0.9996	1	0.3	0.4	0.00006	82.7	3
30	Triadimefon	0.05–0.5	0.9997	0.9	1.1	0.6	0.00007	87.4	3
31	Procymidone	0.05–0.5	0.9995	0.6	0.5	0.6	0.0001	99.5	3
32	Butachlor	0.05–0.5	0.9997	0.7	0.5	0.5	0.0003	89.3	3
33	Dieldrin	0.05–0.5	0.9997	0.7	0.7	0.6	0.00004	85.7	3
34	Endrin	0.05–0.5	0.9996	0.8	0.7	0.5	0.00004	84.6	3
35	Chlorobenzilate	0.05–0.5	0.9983	2.3	1.6	0.3	0.0003	89.5	3
36	*o,p'*- DDT	0.05–0.5	0.9998	1.1	0.8	0.5	0.00007	94.1	3
37-1	Tetramethrin-1	0.05–0.5	0.997	2.2	1.1	2.4	0.0003	85.7	3
37-2	Tetramethrin-2								3
38	Fenpropathrin	0.05–0.5	0.9999	0.9	1.1	0.6	0.0002	90.72	3
39-1	Cypermethrin-1	0.05–0.5	0.997	1.9	0.8	1.1	0.0003	81.7	3
39-2	Cypermethrin-2								3
39-3	Cypermethrin-3								3
39-4	Cypermethrin-4								3
40-1	Fenvalerate-1	0.05–0.5	0.998	1.2	0.6	0.6	0.0003	93.9	3
40-2	Fenvalerate-2								3
41	Deltamethrin	0.05–0.5	0.9994	1.4	0.6	0.6	0.0002	86.6	3

Sample preparation

An apple sample was purchased from a local grocery store. Ten grams of homogenized apple sample were weighed into a 50 mL centrifuge tube, and two ceramic homogenizers were added to the sample. QC samples were spiked with appropriate amounts of spiking solution to yield QC samples with a quantitative concentration of approximately 0.1 mg/kg. Ten milliliters of acetonitrile were added to the tube. An Agilent QuEChERS extraction salt packet (part number 5982-5650) containing 4 g of $MgSO_4$, 1 g of sodium chloride, 1 g of Na-citrate, and 0.5 g of disodium citrate sesquihydrate was added to each centrifuge tube for extraction. An Agilent QuEChERS general fruit and vegetables dispersive SPE 15 mL tube (part number 5982-5056) was used for cleanup. For fruits and vegetables with high pigments and fats, other types of QuEChERS packets are needed for extraction and cleanup. The details of the sample preparation procedure are shown in Figure 2.

Matrix blanks were prepared in the same manner as the samples, except there was no addition of spike solution.



* This is for the recovery test. For matrix blanks, skip this step.
** Using acetone for organophosphorus pesticides, while using hexane for organochlorine pesticides.

Figure 2. Flowchart of the QuEChERS extraction procedure for apple samples.

Results and discussion

Organophosphorus pesticides analysis

The sample matrix has a great influence on the results of pesticide analysis. Figure 3 shows a comparison of pesticide chromatograms in an apple matrix blank and acetone. Blue represents a standard prepared in acetone, while red represents a standard prepared in the apple matrix blank. It shows that for some compounds, using a matrix blank to dilute the working solution can improve the sensitivity, especially for some compounds that are difficult to analyze, such as acephate and methamidophos. Organophosphorus pesticides, particularly polar pesticides such as acephate and methamidophos, tend to have broad peaks or tailing. The peak shapes were also improved in the matrix blank.

Simultaneous primary and confirmation analysis from a single injection was accomplished using a dual-FPD GC system. An Agilent CFT 2-way splitter without make-up device was used in this system. The 54 organophosphorus pesticides were divided into four groups for easy and accurate retention time determination. Figures 4 to 7 illustrate the analyses of groups 1, 2, 3, and 4 organophosphorus pesticide mixtures on the HP-50+ and HP-1 columns.

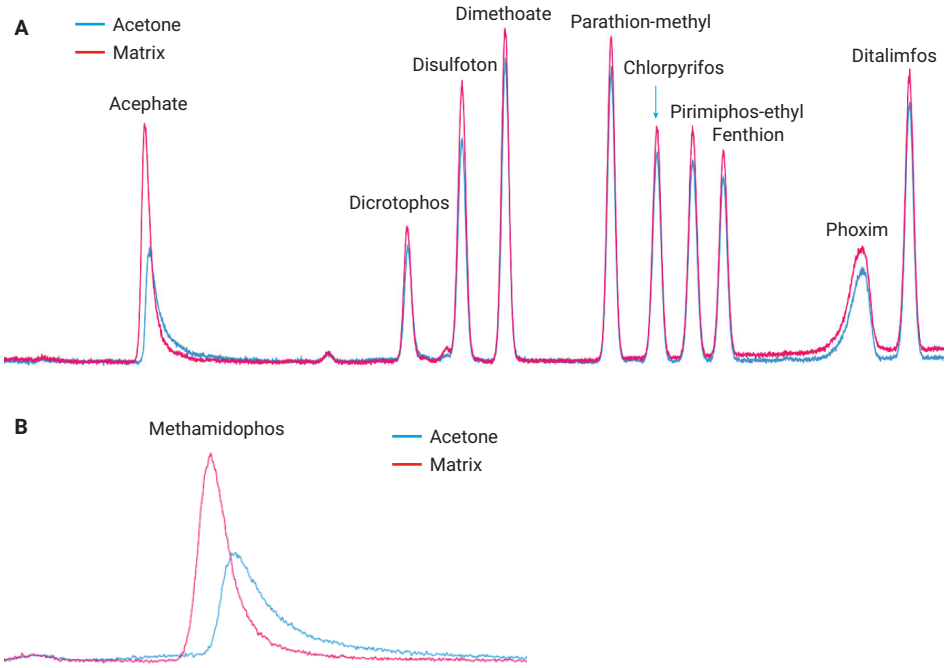


Figure 3. Comparison of chromatograms in apple matrix and acetone (approximately 0.1 mg/ kg) using an Agilent HP-50+ 30 m × 0.53 mm, 1 µm capillary GC column.

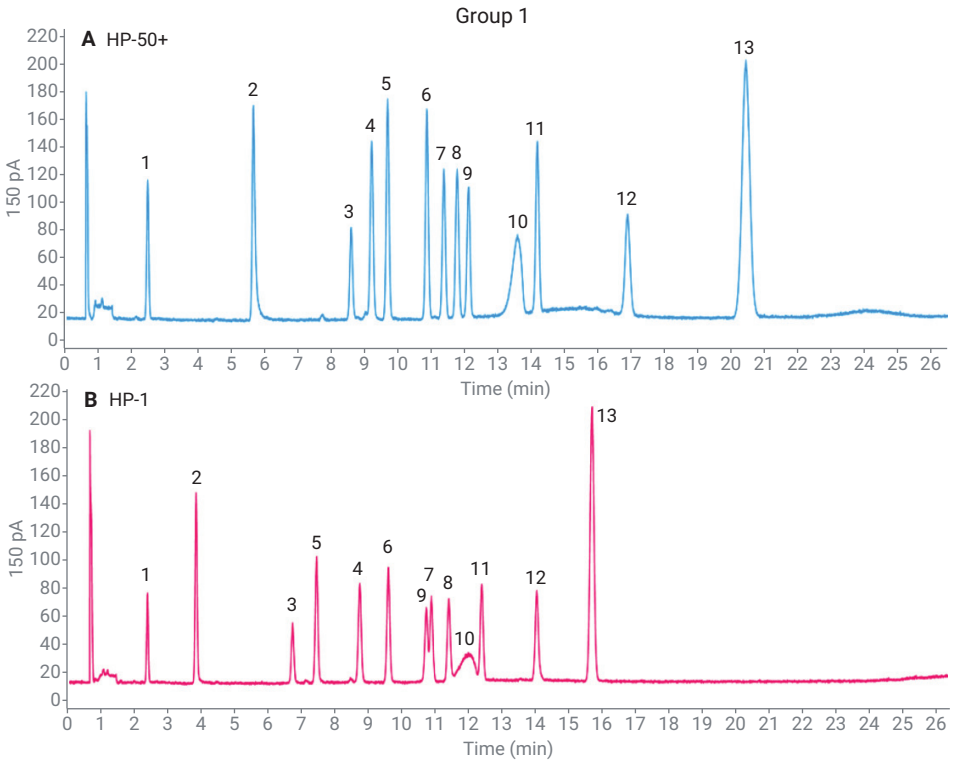


Figure 4. Chromatograms of group 1 organophosphorus pesticide standard solution (approximately 0.1 mg/kg) on a dual-column system using Agilent HP-50+ and HP-1 capillary GC columns.

Matrix-matched calibration standards and spiked QC samples were prepared by spiking appropriate standard solutions into the matrix blank. For 44 compounds analyzed, the linearity range was in the range of 0.05 to 0.5 mg/kg. For other compounds such as phoxim, phosmet, trichlorfon, pyrazophos, and so on, which have low response factor, the linearity range was 0.2 to 2 mg/kg. Table 2 shows the details. Linearity across the range studied gave R^2 values of 0.992 for all the organophosphorus pesticides. Most of them have R^2 values greater than 0.999. Table 2 lists the correlation coefficient for each of the pesticides on an HP-50+ column.

Repeatability assessments at three levels: low, middle, and high were obtained for all compounds in apple matrix. For most compounds, the low level was 0.05 mg/kg, the middle level was 0.1 mg/kg, and the high level was 0.5 mg/kg. For low response value compounds, the low, middle, and high levels were 0.2, 0.4, and 2 mg/kg except naled and phosphamidon. Table 2 shows that the area RSDs were less than 5% for all the compounds, which demonstrated the accurate, precise, and stable performance of this system.

Signal-to-noise ratio (S/N) was used for method detection limit (MDL) calculation. A concentration of the lowest calibration level was used to test the MDL, and the values for all compounds are listed in Table 2.

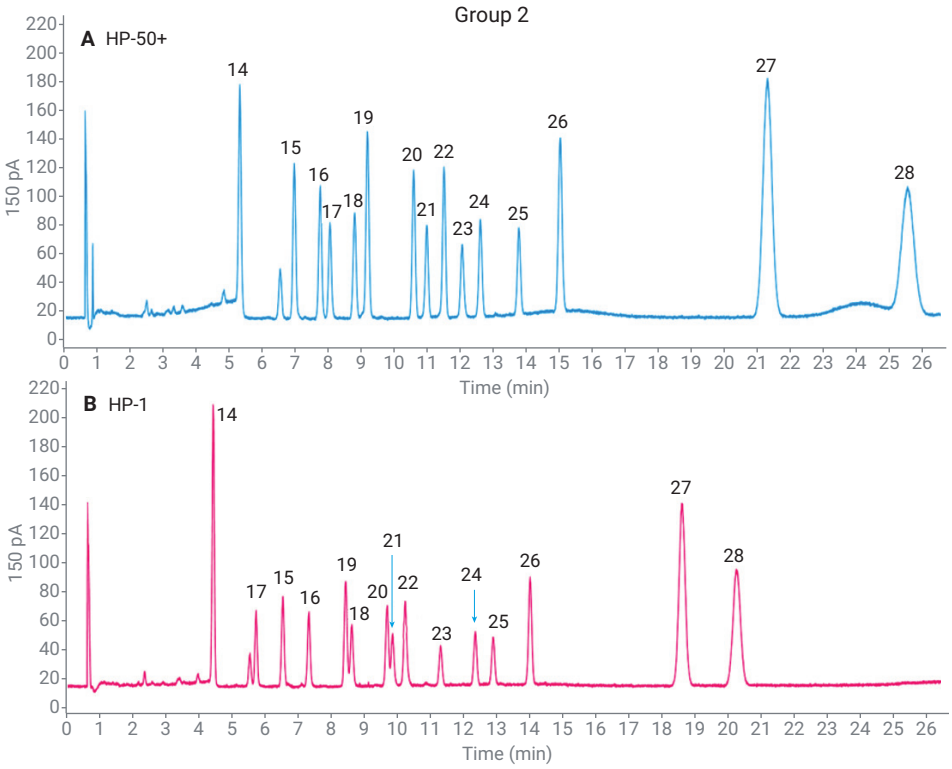


Figure 5. Chromatograms of group 2 organophosphorus pesticide standard solution (about 0.1 mg/kg) on a dual-column system using HP-50+ and HP-1 capillary GC columns.

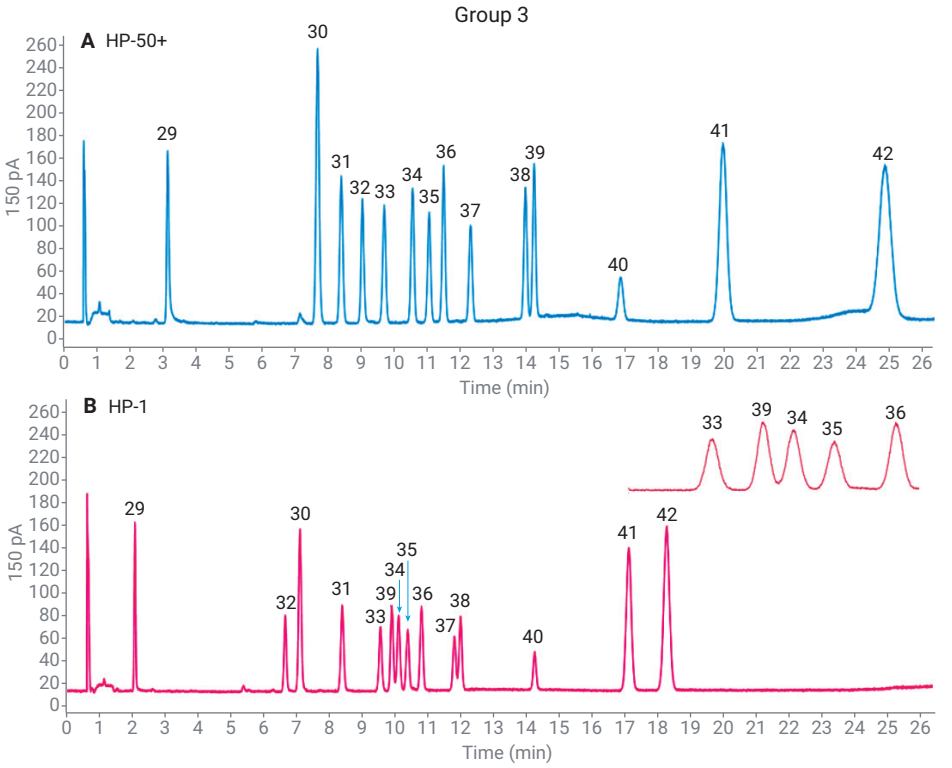


Figure 6. Chromatograms of group 3 organophosphorus pesticide standard solution (about 0.1 mg/kg) on a dual-column system using HP-50+ and HP-1 capillary GC columns.

As described in the Sample preparation section, QC samples were spiked with appropriate amounts of spiking solution to yield QC samples with quantitative concentration of 0.1 mg/kg (for low response value compounds such as phoxim, acquired at the 0.4 mg/kg level). Recoveries were determined on an HP-50+ column, and the results for all organophosphorus pesticides were between 70.4 and 118.2%. Table 2 lists the recoveries for the individual pesticide. Most of the compounds, even the polar compounds such as acephate and methamidophos, have good recovery data due to the excellent extraction and cleanup process of QuEChERS, as shown in Figure 8.

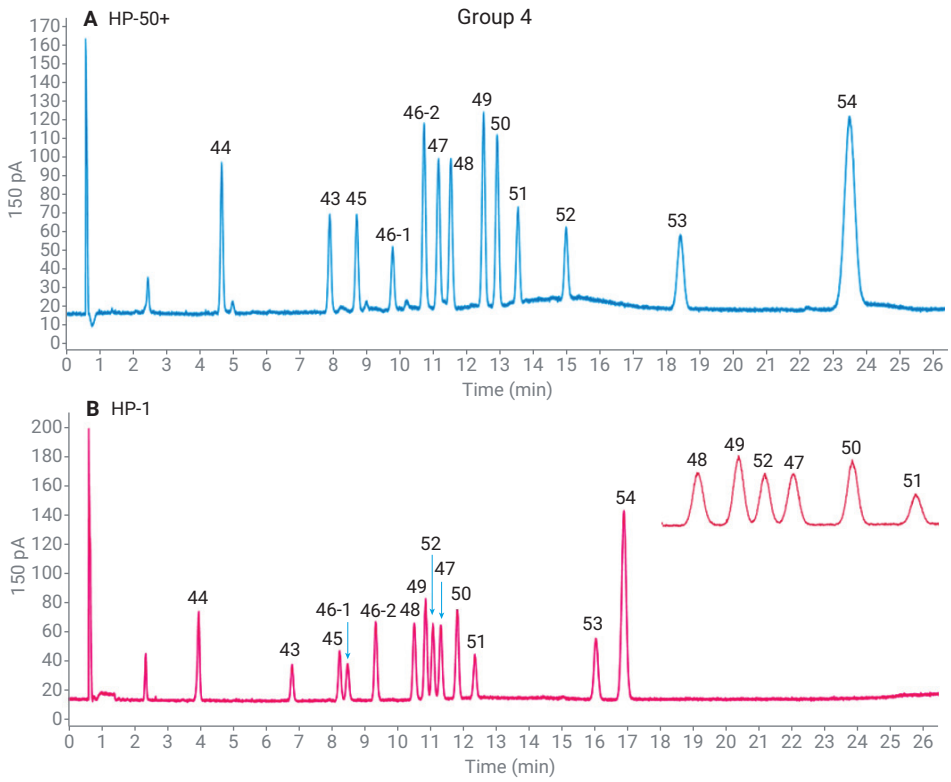


Figure 7. Chromatograms of group 4 organophosphorus pesticide standard solution (approximately 0.1 mg/kg) on a dual-column system using Agilent HP-50+ and HP-1 capillary GC columns.

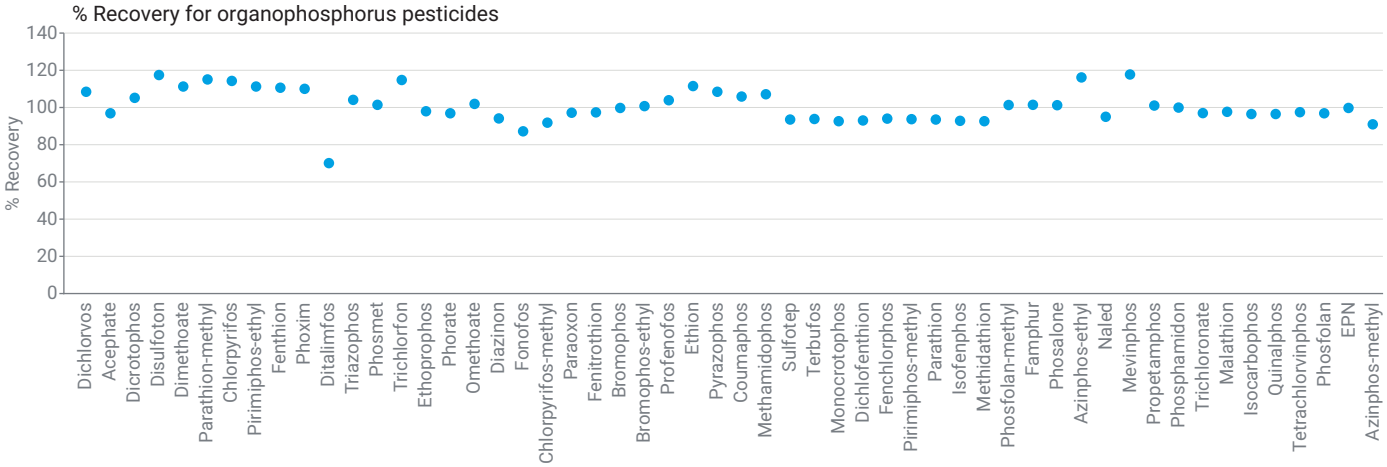


Figure 8. Recovery data of organophosphorus pesticides.

Organochlorine pesticides analysis

Similar to the analysis of organophosphorus pesticides, simultaneous primary and confirmation analysis from a single injection was accomplished using a dual-ECD GC system for organochlorine pesticides analysis. A CFT two-way splitter without make-up device was used in this system. Forty-one organochlorine pesticides were divided into three groups. Figures 9 to 11 illustrate the analysis of groups 1, 2, and 3 organochlorine pesticide mixtures on DB-5 and DB-17 columns.

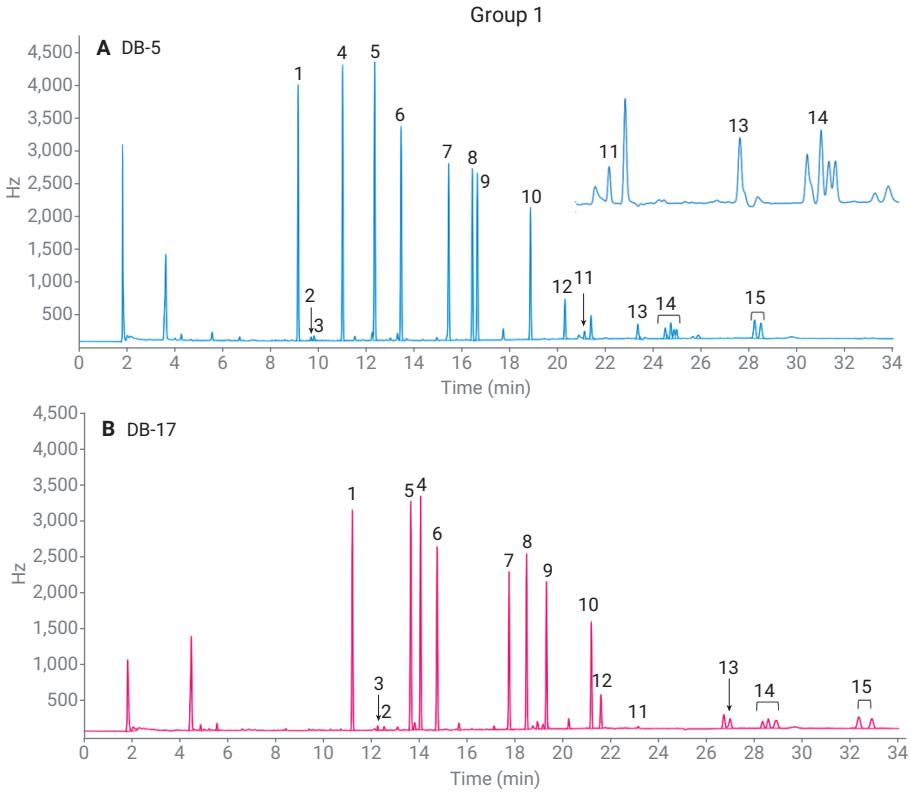


Figure 9. Chromatograms of group 1 organochlorine pesticide standard solution (0.1 mg/kg) on a dual-column system using DB-5 and DB-17 capillary GC columns.

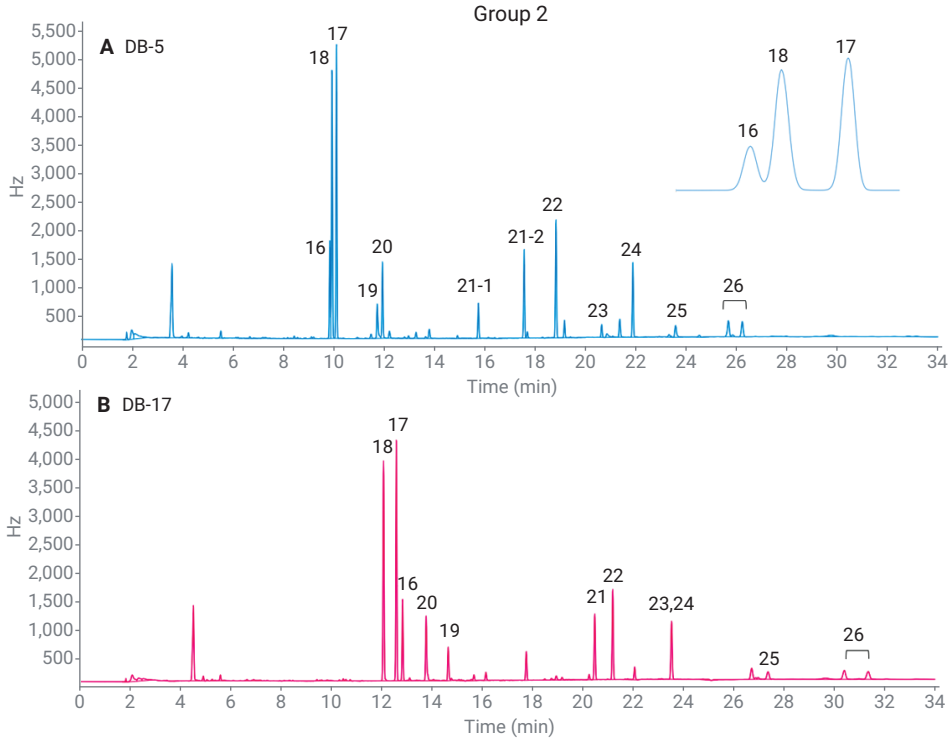


Figure 10. Chromatograms of group 2 organochlorine pesticide standard solution (0.1 mg/kg) on a dual-column system using DB-5 and DB-17 capillary GC columns.

For the analysis of organochlorine pesticides, some compounds such as cyfluthrin and cypermethrin have isomers. The retention times of those isomers were close, and it was difficult to achieve baseline separation, as shown in Figure 12. For these compounds, the setting of integration parameters was particularly important. Because the standards purchased from the vendor were also isomer mixtures, and no other compounds eluted between the isomers, those isomers were integrated as one peak for quantitative analysis. Figure 13 shows that, in OpenLab CDS 2.3 software, the Area Sum function can help integrate the isomers.

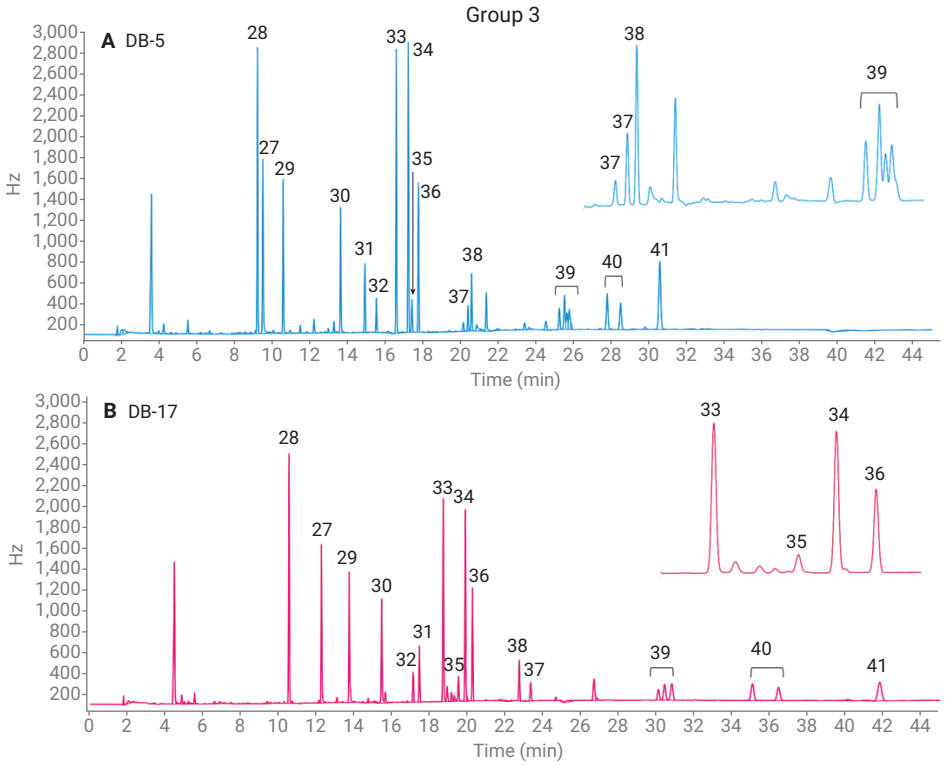


Figure 11. Chromatograms of group 3 organochlorine pesticide standard solution (0.1 mg/kg) on a dual-column system using Agilent DB-5 and DB-17 capillary GC columns.

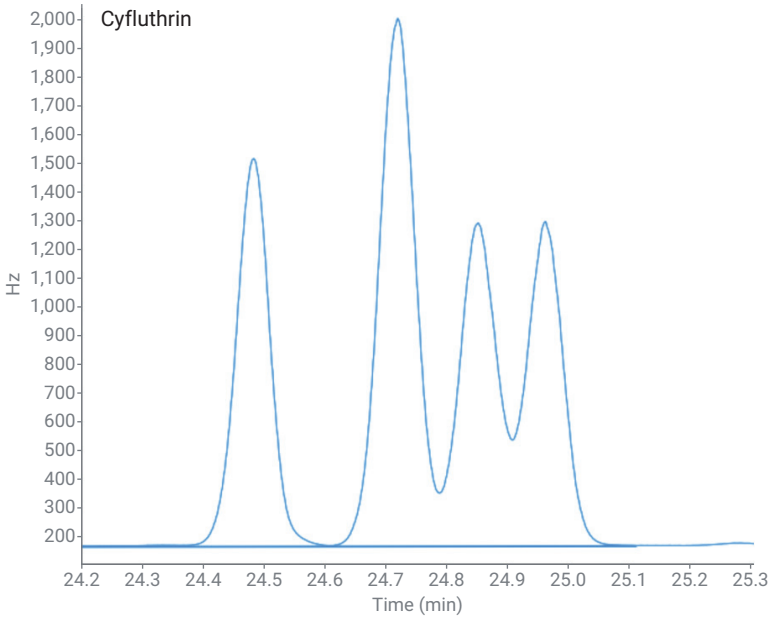


Figure 12. Chromatogram of cyfluthrin isomers using the Area Sum function for integration.

Matrix-matched calibration standards and spiked QC samples were prepared by spiking appropriate standard solutions into the matrix blank. The spiking concentration for calibration standards were between 0.05 and 0.5 mg/kg in apple matrix. The data were processed with OpenLab CDS 2.3 software. Table 3 shows the results on a DB-5 column, the R^2 values >0.991 for all organochlorine pesticides. The area RSD values for eight replicates at three levels were below 4%, with the typical RSD below 2%. Compared to the NY/T 761 method, the optimized extraction and cleanup procedure was validated by running spiked samples at 0.1 mg/kg level. Acceptable recoveries were achieved for most of the analytes. Recoveries were between 77.3 and 118.6%. Table 3 also shows the MDL results for the 41 compounds. S/N was used for MDL calculation. The results were better than the NY/T 761 method reference results.

Global parameters are used for all not specific signals

Use	Time (min)	Event	Value
☑	0.000	Slope sensitivity	1.00000
☑	0.000	Peak width	0.02000
☑	0.000	Area reject	1.00000
☑	0.000	Height reject	50.00000
☑	0.000	Shoulders mode	Off
☑	0.000	Area% reject	0.00000
☑	24.300	Area sum	On
☑	25.100	Area sum	Off
☑	28.050	Area sum	On
☑	28.700	Area sum	Off

Figure 13. Integration table for cyfluthrin isomers.

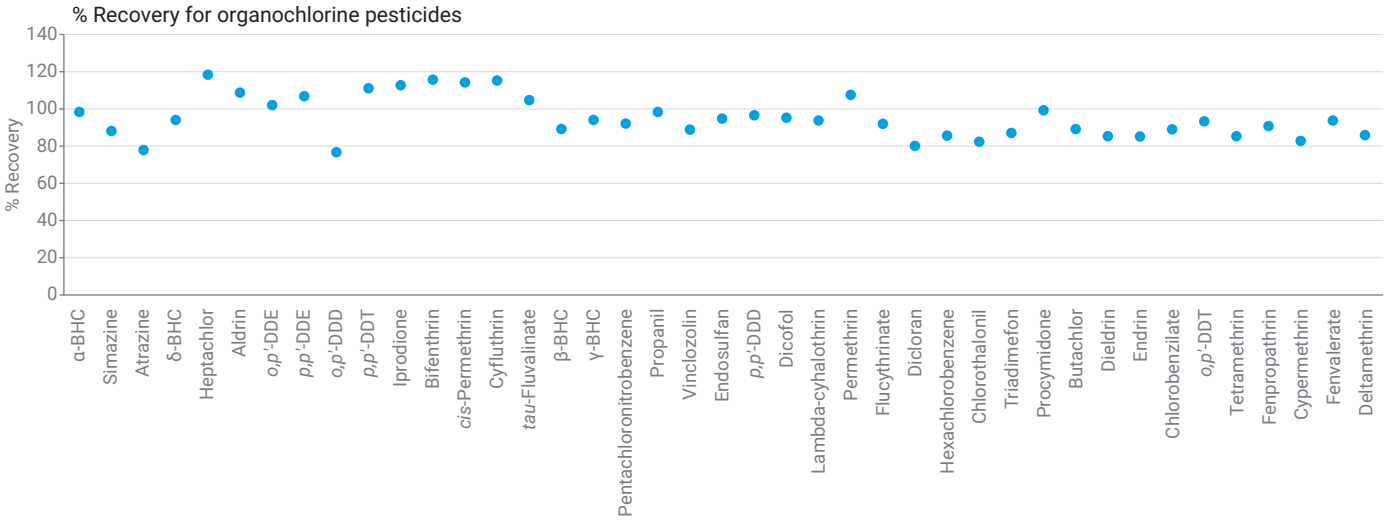


Figure 14. Recovery data of organochlorine pesticides.

Conclusion

An Agilent 8890 GC configured with four detectors (two FPDs and two ECDs) was used to screen organophosphorus and organochlorine pesticides in fruit and vegetables. Splitting the samples into two different columns then to two detectors facilitated selectivity, identification, and confirmation of organophosphorus pesticides and organochlorine pesticides from single injections of each extract, increasing laboratory productivity.

This Application Note demonstrates excellent sensitivity, area repeatability, peak shape, and resolution for both organophosphorus and organochlorine pesticides, which shows that this four-detector system is an ideal platform for the NY/T 761-2008 method.

References

1. China National Standard NY/T 761-2008, Determination of Organophosphorus, Organochlorine, Pyrethroid and Carbamate Residues in Vegetables and Fruits.
2. China National Standard GB/T 19648-2006, Determination of 500 Pesticides and Metabolites Residues in Vegetables and Fruits, Gas Chromatography/Mass Spectrometry Method.
3. China National Food Safety Standard GB 23200.113-2018, Determination of 208 Pesticides and Metabolites Residues in Foods of Plant Origin, Gas Chromatography-Tandem Mass Spectrometry Method.

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