A Blind Study of Pesticides in Vegetables by Agilent Bond Elut QuEChERS Extraction Kits and Agilent 5975T LTM GC/MSD

Application Note

Food Diagnostic

Authors

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Abstract

The analysis of pesticides is important in the field of food detection. In this study, blind added multipesticides in cherry tomato and cucumber were investigated. The Agilent Technologies DRS software, RTL pesticides library, and fast Bond Elut QuEChERS sample preparation allow quick onsite pesticides diagnostics with the transportable Agilent 5975T LTM GC/MSD. This work describes a method for quick identification of target pesticides in vegetables onsite by the transportable Agilent 5975T LTM GC/MSD. This instrument provides the same excellent performance as previous Agilent mass spectrometers.

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Introduction

Pesticide residues are an important concern in the field of food safety. It is now common to analyze for pesticide residues in food samples to track their distribution and ensure a safe food supply. Pesticides used on vegetables and fruits must be monitored to ensure their residues are within a safe range before they go to the market. Performing this analysis offsite causes expensive delays, and successive rounds of sampling, and hinders emergency detections. Many grocery markets have onsite pesticide detectors, which are mostly based on enzyme reactions or fluorescent emissions screen mechanisms. Those detectors cannot give reliable qualitative or quantitative results. GC/MS is a good tool for reliable detection and separation of pesticides. It can produce accurate qualitative and quantitative results but is often limited to a fixed-base lab. If GC/MS could be used in a mobile lab onsite, synchronized sampling and analysis could be carried out expeditiously, providing the rapid pesticides determination. This study proved that the transportable Agilent 5975T LTM GC/MSD has excellent features for use in mobile lab.

Agilent Technologies has excellent tools and reliable solutions for pesticide analysis. Agilent DRS for GC/MS combines the power of Agilent RTL technology, ChemStation quantitation, and NIST's AMDIS function providing a completely automated reporting package that can quantitate and screen pesticides and endocrine disrupters in minutes, rather than hours. The sample pretreatment employs the QuEChERS extraction method with the Agilent Bond Elut QuEChERS EN dispersive kits. Agilent previous MS products provide unmatched performance, sensitivity and accuracy for continuous productivity and reliable results in the laboratory. This application studied blind pesticide identification in two vegetables to illustrate the performance and rapid deconvolution capacity of the Agilent 5975T LTM GC/MSD. A total of 59 pesticides were spiked in cherry tomato and cucumber according to the NY/T 761-2008, Ministry of Agriculture of the People's Republic of China. NY/T 761-2008 regulates about 106 pesticides in vegetable and fruits. Ninety-five pesticides must use a GC as detector. All of the pesticides selected in this application complied with this regulation. This application note used cherry tomato and cucumber as the pesticide matrix to verify the capability of the Agilent 5975T LTM GC/MSD.

Highlights

The highlights of this method are as follows:

- Simple, quick, reliable sample preparation
- Agilent RTL pesticides library and DRS software
- Multi-pesticide presence confirmation within 2–3 min after sample run
- Transportable Agilent 5975T LTM GC/MSD

Experiment

Software Required

G1701EA	GC/MS ChemStation (latest version)
G1716	MSD Deconvolution Reporting Software (Version A.04.00 or newer)
G1033A	NIST08 Mass Spec Library + AMDIS + NIST Library Search
G1672AA	RTL Pesticide Library

Reagents and Chemicals

All reagents were analytical or HPLC grade. The pesticides were purchased from Sigma-Aldrich (St. Louis, MO, USA). The water was from a MilliQ system (Milford, Mass, USA).

Equipment and Material

The analysis was performed on an Agilent 5975T LTM GC/MSD system equipped with an Agilent 7693 automatic liquid sampler (Agilent Techologies, Shanghai, P.R.China). RTL software is a feature of Agilent MSD ChemStation. DRS (A.04.00, p/n G1716AA) was installed. Separation of the compounds was achieved on an Agilent J&W HP-5ms LTM (30 m × 0.25 mm, 0.25 µm). Extraction and cleanup were achieved with an Agilent Bond Elut QuEChERS EN Extraction kit (p/n 5982-5650) and a Bond Elut QuEChERS EN Dispersive SPE kit (p/n 5982-5156).

Instrument conditions

Table 1. Instrumentation and Conditions of Analysis

Instrumentation:	
GCMS system:	5975T LTM
Inlet:	Split/splitless
Autosampler:	Agilent 7693
Column:	Agilent J&W HP-5ms LTM 30 m × 0.25 mm, 0.25 µm
Guard column:	1 m column with same phase as analytical column, connected to the injector.
Experimental conditions:	
Inlet temperature:	280 °C
Injection volume:	1 µL
Injection mode:	Splitless
Carrier gas:	Helium
Head pressure:	26.878 psi, constant pressure mode
Method RTlocked to chlorpyrifos methyl at 16.593 min	
LTM oven temperature:	70 °C (2 min), 25 °C/min, 150 °C (0 min), 3 °C/min, 200 °C (0 min), 8 °C/min, 280 °C (10 min)
Transfer line temperature:	270 °C
MSD interface:	270 °C
Ion source:	230 °C
Quad temperature:	150 °C
Ionization mode:	EI
Scan mode:	Full scan, 50–550 u
EMV mode :	Gain factor
Gain factor :	5.00
Resulting EM voltage:	1129 V
Solvent delay:	3 min

Sample Preparation

Samples

The samples were organic vegetables without pesticides purchased from a supermarket in Shanghai, China. The samples were spiked with different concentration levels of a certain number of pesticides.

Table 2. Sample Details for Blind Study

Sample matrix	Number of pesticides	Conc range (µg/g)	Comments
Cherry tomato	40–59	0.05–1.0	Spiked
Cucumber	46	0.05–1.0	Spiked

Extraction

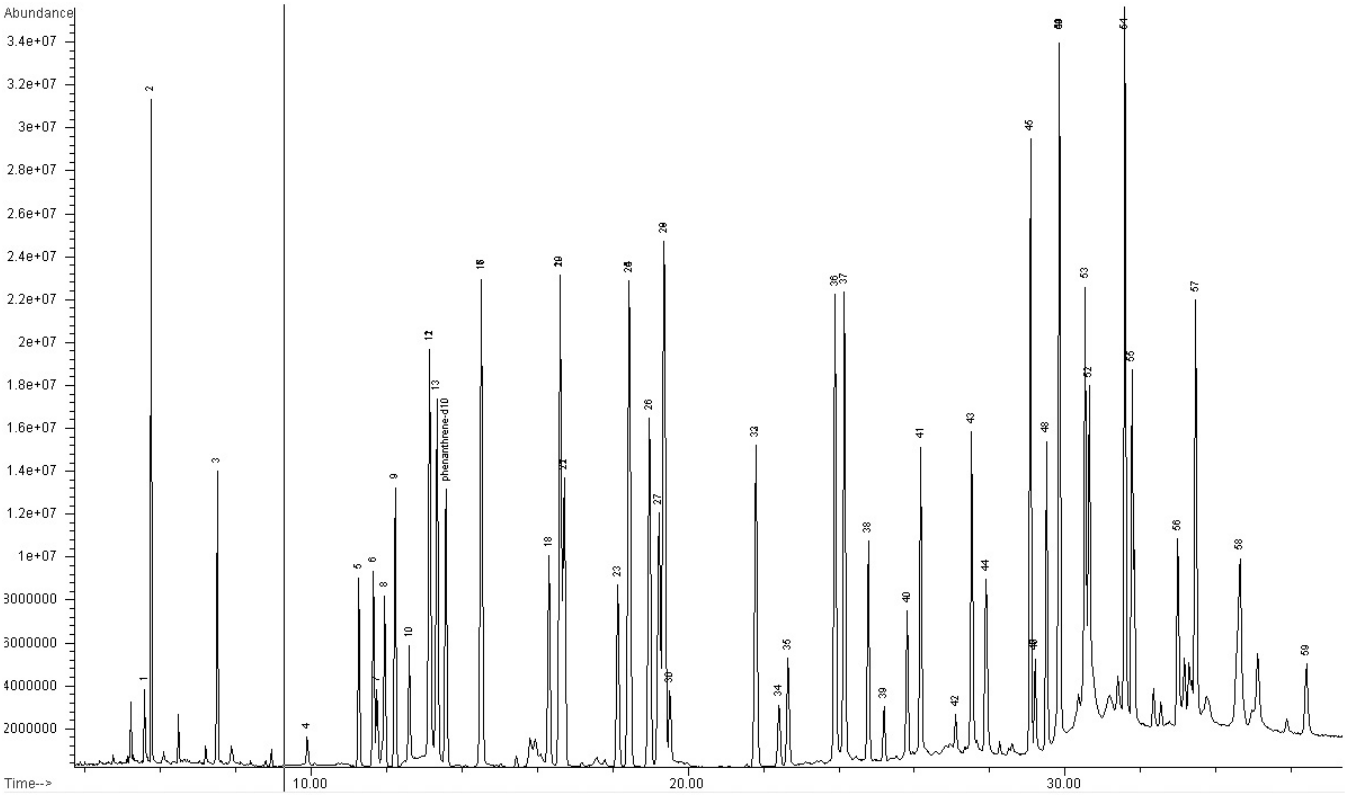
A 5 g sample of vegetable homogenate was placed into a 50 mL centrifuge tube. Five mL of water were added to the tube, and the tube shaken vigorously for 1 min. A 10 mL amount of acetonitrile was then added, shaken vigorously for 30 sec, followed by an Agilent Bond Elut QuEChERS EN extraction packet, which contained 4 g of anhydrous $MgSO_4$, 1 g of anhydrous NaCl, 1 g of NaCitrate, and 0.5 g of disodium citrate sesquihydrate. The sample tubes were hand shaken vigorously for 1 min then further centrifuged at 4000 rpm for 5 min.

Cleanup

A 6.0 mL aliquot of the upper ACN layer was transferred into a Bond Elut QuEChERs EN Dispersive PE 15-mL tube. This tube contained 150 mg of PSA, 150 mg of C18 and 900 mg of anhydrous $MgSO_4$. After one minute of shaking, the tubes were centrifuged at 4000 rpm for 5 min. After a 4-mL aliquot of the extract was filtered through a 0.22 µm filter (p/n 5064-8222), it was ready for analysis.

Results and Discussion

Sample extracts for pesticide residue analysis are usually very dirty because there is the risk of removing pesticides along with endogenous compounds if elaborate cleanup steps are used. However, the sample preparation can remove “dirty” matrices to some degree. In addition, the guard column on the 5975T LTM GC/MSD can remove some of the contamination, and this is easily changed when necessary. Therefore, the transportable 5975T LTM GC/MSD can be a good tool for outside or onsite detection. DRS helps the analyst "see through" the interferences and identify the target compounds; pesticides in this case. A total of 59 pesticides were spiked in cherry tomato and cucumber. Figure 1 shows the total ion chromatogram of the 59 pesticides.



1	Methamidophos	13	Lindane	25	Aldrin	37	p,p'-DDE	49	Phosalone
2	Dichlorvos	14	Pentachloronitrobenzene	26	Malathion	38	Endrin	50	Mirex
3	Mevinphos	15	Phosphamidon I	27	Fenthion	39	Endosulfan (beta isomer)	51	Leptophos
4	Omethoate	16	BHC delta isomer	28	Chlorpyrifos	40	p,p'-DDD	52	lambda.-Cyhalothrin
5	Ethalfluralin	17	Diazinon	29	Parathion	41	Ethion	53	Fenarimol
6	Trifluralin	18	Phosphamidon II	30	Triadimefon	42	p,p'-DDT	54	Permethrin
7	Monocrotophos	19	Chlorpyrifos Methyl	31	Isodrin	43	Hexazinone	55	Coumaphos
8	BHC alpha isomer	20	Methyl parathion	32	Quinalphos	44	Propargite	56	Cypermethrin
9	Hexachlorobenzene	21	Vinclozolin	33	Isofenphos	45	Iprodione	57	Ethofenprox
10	Dimethoate	22	Heptachlor	34	Methidathion	46	Bifenthrin	58	Fenvalerate
11	Atrazine	23	Fenitrothion	35	Endosulfan (alpha isomer)	47	Fenpropathrin	59	Deltamethrin
12	BHC beta isomer	24	Pirimiphos-methyl	36	Dieldrin	48	Tetradifon		

Figure 1. Total ion chromatogram (TIC) of 59 pesticides.

Linearity and Recovery Tests for Targets in Cherry Tomato and Cucumber

The recovery was evaluated for spiked samples at three different levels. The analysis was performed in replicates of two at each level to test the repeatability of the sample preparation. The levels were 0.05, 0.1, 0.5 µg/mL and recovery was 79.0 to 118%, with the exception of the pesticides that exceeded the detection limit.

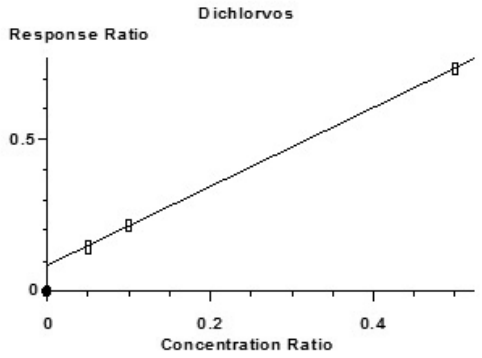


Figure 2. Dichlorvos in cucumber matrix.

The linear calibration curves were obtained by plotting the peak area for each analyte versus its concentration. Curves were generated by spiking the sample blanks at a concentration range of 0.05–0.5 µg/mL. The linearity coefficient of the tested pesticides was greater than 0.995. Figure 2 is an example of the calibration curve.

Blind Study of Pesticides in Cherry Tomato and Cucumber

Different levels of target pesticides were spiked into cherry tomato and cucumber before sample preparation to evaluate the number of pesticides detected. It required 2–3 minutes to screen 928 compounds automatically in each sample with the RTL pesticides library and DRS software.

Different concentrations of pesticides from 0.5 µg/g to 1.0 µg/g were then added to the cherry tomato and cucumber. All levels were found by the DRS pesticides method. MSD ChemStation identified the targets according to 3–4 ions of each compound, and provided the quantitative results. Many low level pesticides can be read by DRS but not ChemStation. Because the quant base is customized, 95% of the added pesticides can be identified by ChemStation after manually modifying the quant database of target pesticides. Table 3 shows the DRS results of cherry tomato matrix.

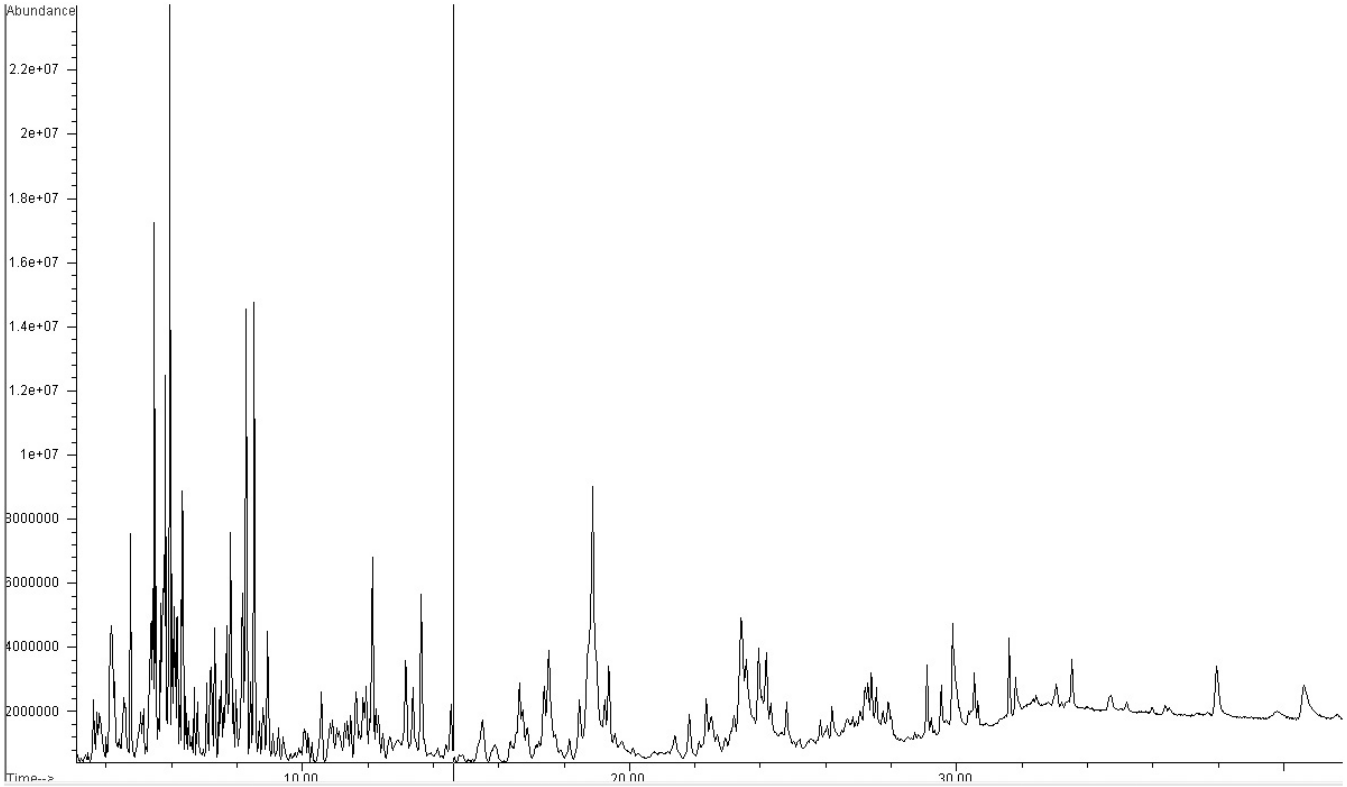


Figure 3. A 0.2 to 1.0 µg/g amount of pesticide spiked in cherry tomato. All of the targets could be found by DRS software within 2 min.

Table 3. Partial DRS Results of Cherry Tomato Analysis

			Amount (ng)		AMDIS		NIST	
RT	Cas number	Compound name	ChemStation	AMDIS	Match	R.T. Diff sec.	Reverse Match	Hit Number
5.6755	10265926	Methamidophos	0.38		72	1.2	83	1
5.7722	62737	Dichlorvos	0.13		95	–3.5	90	1
7.5277	7786347	Mevinphos	2.55		96	–4.0	80	1
11.2899	55283686	Ethalfluralin	0.77		94	0.4	87	1
11.6607	1582098	Trifluralin	1.3		93	1.4	86	1
11.7711	6923224	Monocrotophos	0.1		83	2.0	80	1
13.1776	1912249	Atrazine	0.7		94	1.1	85	1
24.7983	72208	Endrin	0.06		91	3.2	90	1
25.214	33213659	Endosulfan (beta isomer)	0.1		87	4.0	81	2
25.8277	72548	p,p'-DDD	0.13		97	0.5	91	1
27.919	2312358	Propargite	1.65		86	2.3	89	1
29.5230	116290	Tetradifon	0.08		95	8.6	88	2
29.8285	2310170	Phosalone	0.32		85	9.1	80	1
29.8709	2385855	Mirex	0.66		77	2.2	82	1
31.6063	52645531	Permethrin I	0.2		96	0.2	91	3
31.8530	56724	Coumaphos	1.03		89	0.2	80	1
33.5186	80844071	Ethofenprox	0.4		93	–0.1	92	1
35.9745	52918635	Deltamethrin			44	–1.6	64	1
36.506	52918635	Deltamethrin	0.05					
13.636		Phenanthrene-d10						

Conclusion

The Agilent RTL and DRS software combined with simple sample preparation allows onsite detection using the transportable Agilent 5975T LTM GC/MSD. This application also describes a well-developed sample preparation method as the primary means of removing much of the matrix interference. QuEChERS was employed to simplify the sample preparation procedure and improve mobile lab detection capability. The easily-changed LTM guard column on the Agilent 5975T LTM GC/MSD is an alternate way to keep the analytical column clean.

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