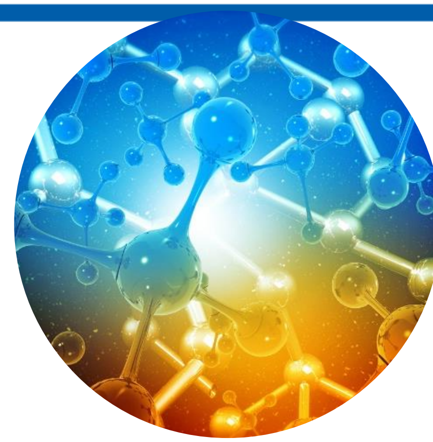

TN-2100

Development of a New Analytical Method for Determining Pesticide Residues by Gas Chromatography-High Resolution Mass Spectrometry using the Zebron™ ZB-5MS*PLUS*™ Column

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Introduction

Foods of plant origin, fresh or processed ones, may contain pesticide residues due to agricultural practices. Food safety control is highly relevant for the protection of consumers and therefore, pesticide residues are regulated by governments and professional associations. Maximum residue limits (MRLs) establish the maximum allowed amount of pesticides in fruits and vegetables to be consumed. For evaluating such accomplishment with regulations and legislations and ensuring consumer´s safety, reliable and powerful analytical methodologies are demanded.

Traditionally, chromatographic techniques have been used in combination with mass spectrometry as a detection system in control laboratories. In this sense, tandem mass spectrometry (MS/MS) using triple quadrupole (QqQ) technology has been widely used for pesticide residue determination. In general, it provides good sensitivity and selectivity allowing the detection of several pesticides (typically between 150-200) in one single run. For that, a target analysis strategy is applied limiting the number of compounds to be under analytical control. However, in order to increase the ability to detect a greater number of compounds in complex matrices, high resolution mass spectrometry (HRMS) coupled to chromatographic techniques is increasingly being incorporated to routine work-flow laboratories because of its power to discriminate analytical information and capability to avoid matrix interferences. Recent instruments have significantly improved robustness, sensitivity and selectivity. Thanks to these properties and its capability to work in untargeted analysis mode, HRMS can be used for developing analytical methods with a larger number of pesticides under control and with the possibility of detecting new compounds or metabolites without significant modifications. It provides methodologies without limitations on the number of analytes that can be monitored in one run. The use of full scan mode is of great potentiality because of its ability to perform retrospective analysis searching in the raw data obtained.

HRMS instruments present high capability for unequivocal identification of compounds thanks to the measurement of accurate mass. In this sense, the combination of gas chromatography (GC) with HRMS is a very powerful tool together with nominal spectral libraries for screening purposes. In this technical note, we show the capabilities of the Zebron ZB-5MS*PLUS* columns in separating residual pesticides by coupling GC with HRMS. The ZB-5MS*PLUS* stationary phase provides a deactivated silica surface and a 5 % phenyl-arylene selectivity that provides the best peak shape for challenging pesticide compounds. Such methodology may have a higher impact on users than a traditional one based on low resolution mass spectrometry.

Sample Preparation

Fruit and vegetable samples used during development and validation of the method, as well as the rest of the samples used for the non-target analysis, were purchased directly from local markets in the city of Almería (Spain). Samples were chopped and homogenized according to the method established in Directive 2002/63/EC. Samples were processed following a citrated buffered roQ™ QuEChERS protocol (KS0-8909).

Briefly, a 10 g portion of sample was weighed in a 50 mL polypropylene centrifuge tube. 10 mL of acetonitrile was added to the sample, and this was vortexed for 2 min. Afterwards, 4 g of magnesium sulfate, 1 g of sodium chloride, 1 g of trisodium citrate dehydrate, and 0.5 g of sodium hydrogencitrate sequihydrate were added. The sample was vortexed for 2 min. The tube was centrifuged for 6 min at 5000 rpm (4136 x g). Then, a clean-up step was carried out. For this, 5 mL of the extract was transferred to a 15 mL centrifuge tube containing 750 mg of magnesium sulfate and 125 mg of PSA. The sample was again vortexed for 1 min. The tube was then centrifuged for 5 min at 3700 rpm (3601 x g). Finally, a 1 mL aliquot of the clean extract was evaporated with a nitrogen stream to dryness and re-dissolved with 950 µL of ethyl acetate and 50 µL of propoxur-d7. The final extract contained 1 g of sample per mL of extract.

Individual pesticide standard stock solutions were prepared in a suitable solvent (mostly ethyl acetate or acetonitrile) at a concentration of 1000 mg/L and were stored in amber screw-capped glass vials in the darkness. From individual pesticide standard stock solutions, three mix-standards were prepared in ethyl acetate and used for the calibration, as needed. Injection internal standard (propoxur-d7) was added to all prepared vials at 25 µg/L final concentration. Stock and intermediate solutions were stored at -20 °C.

GC-MS Conditions

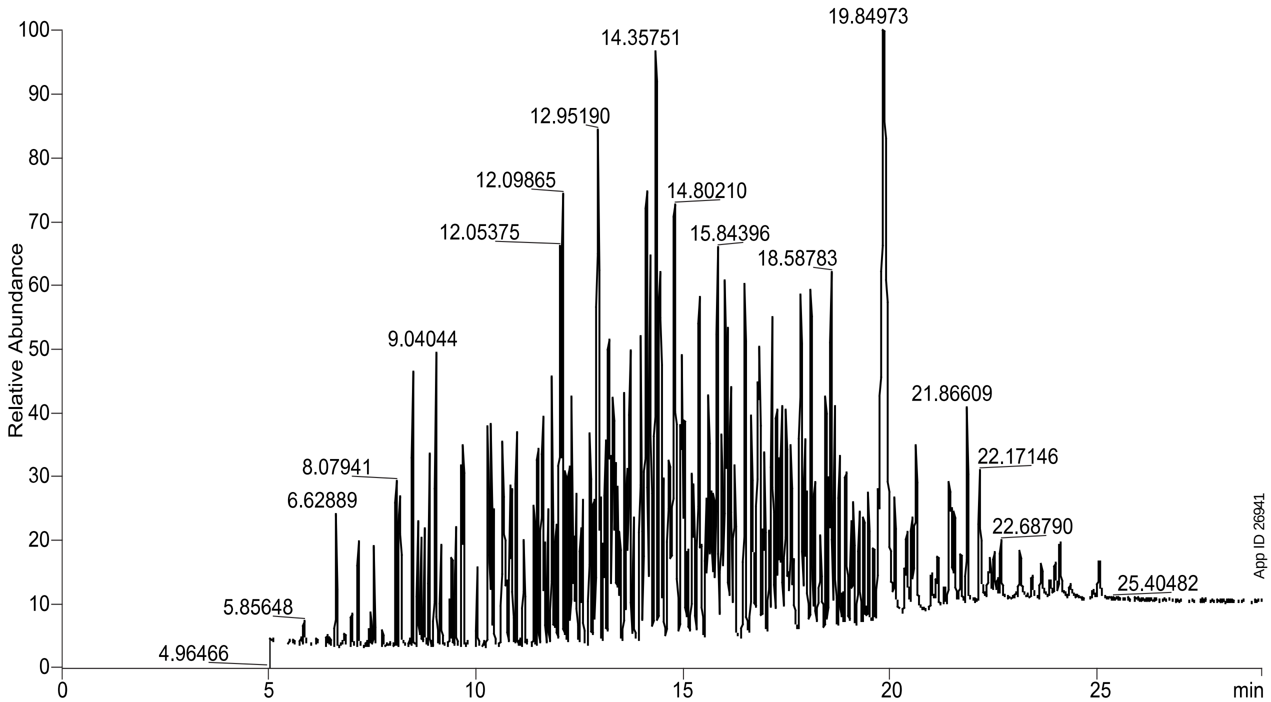
Column:	Zebron ZB-5MS*PLUS*		
Dimension:	30 meter x 0.25 mm x 0.25 µm		
Part No.:	7HG-G030-11		
Injection:	Splitless @ 280 °C, 1 µL		
Carrier Gas:	Helium @ 1 mL/min (Constant Flow)		
Oven Program:	**Ramp(°C/min)**	**Temp (°C)**	**Time(min)**
	-	50	1.0
	20	170	0.0
	10	310	8.0
Detector:	GC-MS		
Detector Temperature:	250 °C		

Table 1. Retention Profile and m/z of 268 Pesticides Included in the Developed Method on a Zebron™ ZB-5MS*PLUS*™ GC Column

Compound Name	RT	m/z 1	m/z 2	m/z 3	Compound Name	RT	m/z 1	m/z 2	m/z 3	Compound Name	RT	m/z 1	m/z 2	m/z 3
Methamidophos	7	95.01	141.00	125.98	Terbutryn	13.65	170.05	185.07	226.11	o,p –DDT	16.93	235.01	199.03	237.00
Dichlorvos	7.16	127.02	184.98	109.01	Fenitrotion	13.69	260.01	124.98	277.02	Aclonifen	16.94	264.03	182.06	194.05
Thiofanox	7.47	161.09	61.01	83.07	Bromacil	13.7	204.96	206.96	230.98	Benodalil	17.08	230.93	202.94	76.03
4-Chloro-3-methylphenol	7.54	142.02	107.05	77.04	Malathion	13.81	127.04	173.08	142.99	Triazophos	17.1	161.06	91.04	285.03
Diclobenilo (Benzonitrile, 2,6-dichloro-)	8.08	170.96	164.00	100.02	Metolachlor	13.98	238.10	240.10	211.08	Sulprofos	17.15	156.01	140.03	112.93
EPTC (Eptam)	8.15	128.11	132.08	160.08	Chlorpyrifos – ethyl	13.99	196.92	257.89	313.96	Tetrasul	17.16	251.96	323.89	175.92
Nicotine	8.16	84.08	133.08	161.11	Thiobencarb	14.05	100.08	125.02	257.06	Famfur (Fonofos)	17.26	124.98	217.01	92.99
2,4,6-trichlorophenol	8.18	195.92	197.92	96.98	Fention	14.08	278.02	169.01	124.98	Trifloxystrobin	17.26	172.04	145.03	222.08
Bifenilo	8.47	154.08	152.06	76.03	DCPA (Clortal dimetil)	14.11	300.88	331.90	272.89	Benalaxyl	17.32	148.11	176.11	206.12
3,5-Dichloroaniline (3,5-Dichlorobenzenamine)	8.6	160.98	126.01	91.04	Fenpropimorph	14.12	128.11	173.11	117.07	Norflurazon	17.35	173.03	145.03	303.04
Mevinphos	8.68	127.02	164.02	192.02	Isomethiozin	14.12	225.08	198.07	184.05	Carbophention	17.4	156.99	124.98	295.99
Butilate	8.76	57.07	146.06	156.14	Parathion	14.15	96.95	109.01	291.03	Cianofenfos	17.4	156.99	169.04	141.01
Clormefos	8.88	121.04	96.95	154.02	Tetraconazole	14.15	336.05	170.98	158.98	Edifenphos	17.47	109.01	201.01	110.02
Etridiazol	9	182.92	210.95	139.91	Aldrin	14.2	262.86	292.93	219.98	Quinoxyfen	17.49	237.06	272.03	112.03
Propham	9.01	93.06	137.05	179.09	Triadimefon	14.2	208.03	85.07	128.00	Clodinafop-propargyl	17.5	238.01	266.04	349.05
1,4-Dimetilnaftaleno	9.04	156.09	141.07	142.07	Anthraquinone	14.21	180.06	76.03	207.04	Lenacile	17.51	153.07	110.06	154.07
Phthalimide	9.16	147.03	103.04	76.03	Isocarbophos	14.23	136.00	121.03	230.00	Propiconazole	17.55	172.96	259.03	190.97
1,2,3,6-Tetra-hydrophthalimide (CIS)	9.37	79.05	151.06	123.07	Nitrothal isopropyl	14.23	194.01	212.02	236.06	Endosulfan sulfato	17.6	271.81	236.84	228.90
Crimidine	9.52	142.03	156.03	171.06	Butralina	14.33	266.11	250.12	190.11	p,p´-DDT	17.62	235.01	165.07	199.03
2-phenylphenol	9.66	169.06	170.07	141.07	4,4-Diclorobenzofenon	14.34	138.99	249.99	251.99	Fenhexamid	17.64	97.10	176.97	266.09
Pentachlorobenzene	9.7	214.88	212.88	177.91	Pirimifos-ethyl	14.35	168.06	180.11	318.10	Hexazinone	17.68	171.09	83.02	128.08
Epsilon-HCH	9.79				Trichloronat	14.36	108.99	268.94	296.97	Diflufenican	17.82	266.04	246.04	218.04
Heptenophos	10.04	89.04	124.01	215.05	Isobenzan	14.43	103.00	310.83	374.80	Methoxychlor	17.82	227.11	169.05	212.08
Clorfenprop metil	10.29	125.02	165.01	196.03	Bromophos-methyl	14.46	330.88	315.85	328.88	Diclofop-methyl	17.83	252.98	281.01	120.06
Tecnazene	10.33	202.88	107.98	177.91	Fenson	14.46	77.04	141.00	268.00	Fenarimol	17.85	138.99	107.02	219.03
Fenobucarb	10.37	150.10	103.05	135.08	Isopropalin	14.49	280.13	238.08	264.13	Nuarimol	17.85	138.99	235.03	203.06
Propoxur	10.38	110.04	152.08	81.03	Isofenphos-methyl	14.53	199.02	121.03	230.99	Fluotrimazole	17.86	165.07	311.10	233.06
Propachlor	10.43	120.08	176.11	93.06	Pendimethalin	14.64	252.10	162.08	191.07	Propargite	17.87	135.08	173.10	107.05
Difenilamina	10.66	169.09	167.07	141.07	Fipronil	14.66	366.94	212.95	254.97	Tebuconazole	17.88	125.02	250.07	163.03
Etoprofos	10.68	157.96	96.95	127.00	Cyprodinil	14.67	224.12	210.10	77.04	Piperonylbutoxide	17.95	176.08	193.09	177.09
Ethalfluralin	10.69				Metazachlor	14.72	81.05	133.09	132.08	Resmethrin	17.99	123.12	171.08	81.07
Cicloato	10.73	154.12	83.09	186.09	Clozolinato	14.76	187.98	331.00	123.99	Mefenpyr-diethyl	18.09	299.04	252.99	327.03
Trifluralin	10.83	264.02	306.07	248.03	Penconazole	14.78	158.98	248.09	160.97	Zoxamida	18.12	258.05	158.98	242.01
Clorprofam	10.85	127.02	171.01	213.06	Isodrin	14.8	192.94	262.86	146.98	Spiromesifen	18.18	272.14	99.08	254.13
Benfluralin	10.88	292.05	264.02	276.06	Isofenphos	14.8	185.00	213.03	121.03	Fenamifos sulfóxido	18.2	304.08	196.08	122.04
Sulfotep	10.98	322.02	237.93	201.99	Clorfenvinphos	14.83	266.94	323.00	294.97	Fenamifos sulfona	18.28	292.04	320.07	214.06
Cadusafos	11.16	158.97	130.94	157.96	Pyrifenox	14.85	262.01	186.96	170.96	Iprodione	18.3	314.01	244.99	316.01
Hexaclorociclohexano-alfa	11.41	180.94	182.93	218.91	Tolylfluanid	14.86	137.03	237.97	239.90	Pyridaphenthion	18.31	199.09	96.95	340.06
Benzene, hexachloro	11.5	283.81	248.84	281.81	Heptacloro-epoxido-A-endo (cis)	14.95	352.84	262.86	236.84	Bifenthrin	18.46	181.10	166.08	165.07
Thiometon	11.5	88.03	124.98	60.00	Phenthoate	14.95	121.01	273.99	245.99	Tetramethrin	18.52	164.07	123.12	79.05
Pentachloroanisole	11.58	236.84	264.84	279.86	Quinalphos	14.98	146.05	157.08	118.05	Phosmet	18.53	160.04	133.03	161.04
Quintozene	11.58	236.84	213.87	141.94	Furalaxyl	14.99	95.01	242.12	152.07	Endrin ketone	18.57	316.90	314.91	344.90
Dicloran (Botran)	11.62	175.97	123.99	205.96	Heptacloro-epoxido-B-exo (trans)	15.04	236.84	252.90	352.84	Fenoxycarb	18.57	88.04	116.07	186.07
Etoxiquina	11.63	202.12	174.09	145.09	Procymidone	15.04	96.06	283.02	255.02	Piperophos	18.58	140.11	122.10	97.09
Simazina	11.67	186.05	173.05	158.02	Triadimenol	15.04	168.11	128.00	208.03	Bifenazato	18.59	199.10	258.10	184.08
Atrazine	11.74	200.07	202.07	173.05	Prallethrin	15.12	123.12	81.07	77.04	Bromopropilate	18.6	340.90	182.94	184.94
Hexaclorociclohexano-beta	11.83	180.94	182.93	218.91	Chlorflurenol-methyl	15.22	215.03	217.02	151.05	Fenpropatrina	18.67	181.06	265.07	209.08
Terbumeton	11.83	210.14	169.10	154.07	Bromophos-ethyl	15.26	302.85	358.91	241.87	Tebufenpyrad	18.78	171.03	318.14	276.09
Profluralin	11.86	318.07	330.11	186.04	Methidation	15.29	145.01	85.04	124.98	Bifenox	18.86	340.99	173.02	309.97
Terbuthylazine	12.01	214.09	173.05	216.08	Tetrachlorvinphos	15.37	330.93	127.02	328.93	Fenazaquin	18.93	145.04	160.13	117.07
Cyanophos	12.04	124.98	227.99	211.99	Flumetralin	15.38	143.01	156.99	404.04	Phenothrin	19.07	123.12	183.08	81.07
Hexaclorociclohexano-delta	12.04	180.94	182.93	218.91	2,4-DDE (o,p DDE)	15.4	246.00	248.00	176.06	Tetradifon	19.12	158.97	226.89	139.01
Benzyl benzoate	12.05	105.03	91.05	77.04	Chlordane (CIS)	15.41	372.83	374.82	236.84	Phosalone	19.23	182.00	121.04	96.95
Terbufos	12.05	57.07	230.97	103.06	Chinomethionate	15.44	206.00	233.99	116.05	Leptophos	19.27	171.00	376.90	155.03
Propyzamide	12.08	172.96	144.96	240.00	Mepanipyrim	15.56	222.10	207.08	77.04	Clortion	19.31	108.99	124.98	127.97
Diazinon	12.09	137.07	179.12	199.06	Ditalimfos	15.61	130.03	242.98	148.04	Pyriproxyfen	19.37	136.08	96.04	226.10
Fluchloralin	12.09	264.02	306.07	326.02	Fenamifos	15.64	154.04	303.11	260.05	Lambda Cyhalothrin	19.48	181.06	141.05	197.03
Fonofos	12.17	108.99	137.02	246.03	Endosulfan beta	15.67	271.81	236.84	169.97	Acrinathrin	19.61	181.06	208.08	152.06
Pyrimethanil	12.25	198.10	183.08	118.05	Napropamide	15.74	72.08	128.11	100.08	Pyrazophos	19.71	221.08	232.11	265.09
Chlorothalonil	12.31	265.88	263.88	132.97	Fludioxonil	15.76	248.04	127.04	154.05	Mirex	19.86	271.81	236.84	269.81
Tefluthrine	12.32	177.03	141.05	197.03	Fipronil sulfone	15.79	254.97	212.95	177.98	Fenoxaprop-P-ethyl	20.12	288.04	261.02	361.07
Terbacil	12.35	161.01	117.00	75.97	Iodofenphos	15.8	376.87	124.98	258.86	Bitertanol	20.36	170.07	168.11	280.11
Disulfoton	12.38	88.03	153.01	185.99	Clorfenson	15.83	174.96	128.11	111.00	Phenisopham (Carbamic acid, ethylphenyl-, 3-[[(1-methy	20.41	148.08	120.08	282.10
Etrimfos	12.43	153.07	181.10	292.06	Hexaconazole	15.84	82.04	231.03	256.00	Permethrin	20.53	183.08	163.01	127.03
Lindane-gamma	12.53	180.94	182.93	218.91	Isoprothiolane	15.84	117.99	161.98	188.97	Fluquinconazol	20.58	340.04	313.03	286.02
Pirimicarb	12.58	166.10	72.04	238.14	Prothiofos	15.84	112.93	161.96	308.99	Pyridaben	20.62	147.12	117.07	309.08
Benoxacor	12.77	120.04	176.07	224.05	Profenofos	15.92	207.91	336.97	266.89	Proclhoraz	20.63	180.11	308.00	70.03
Formothion	12.77	93.01	142.99	110.97	Oxadiazone	15.94	174.96	258.03	302.02	Cinidon-ethyl	20.64	331.01	179.98	123.99
Bromocyclen	12.85	236.84	356.80	358.80	Oxyfluorfen	16.02	252.04	300.00	317.01	Butafenacil	20.65	331.01	179.98	123.99
Endosulfan alfa	12.85	236.84	169.97	276.87	p,p´-DDE	16.02	246.00	176.06	315.94	Fenbuconazol	21	129.06	198.09	125.02
Pentachloroaniline	12.91	264.86	262.86	191.92	Myclobutanil	16.05	179.02	150.01	245.06	Cyfluthrin	21.16	206.06	199.06	163.01
Benfuresate	12.94	163.08	135.08	145.06	Bupirimato	16.07	208.14	193.14	273.10	Cypermethrin	21.32	181.06	209.08	152.06
Etofumesato 2-keto	12.95	149.06	177.06		Kresoxim-methyl	16.09	116.05	131.07	206.08	Halfenprox	21.43	262.99	183.05	264.99
Diclofention	12.96	222.94	279.00	161.96	Buprofecina	16.14	105.06	175.09	249.11	Boscalida	21.47	139.99	342.03	111.99
Endosulfan ether	12.96	276.87	306.88	271.91	p,p´-DDD	16.18	235.01	165.07	199.03	Flucythrinate	21.49	157.05	199.09	181.06
Propanil	12.97	160.98	162.98	217.01	Dieldrin	16.23	262.86	236.84	276.91	Quizalofop-ethyl	21.56	299.06	163.01	136.05
Chlorpyrifos – methyl	13.09	285.93	124.98	78.99	Cyflufenamid	16.26	223.03	118.04	412.12	Pyridalyl	21.7	204.06	164.03	148.04
Plifenat	13.13	216.98	241.90	257.90	Clorfenapir	16.27	247.05	363.94	137.00	Silafluofen	21.87	179.09	286.12	276.10
Vinclozoline	13.14	178.04	212.00	197.99	Cyproconazole	16.48	222.04	138.99	125.02	Flumioxazin	22.38	354.10	259.05	287.08
Transfluthrin	13.2	163.02	127.03	143.01	4,4-Dibromobenzophenone	16.49	182.94	154.95	76.03	Esfenvalerato	22.42	125.02	225.08	167.06
Parathion-methyl	13.21	124.98	263.00	109.01	Perthane	16.5	223.15	167.09	178.08	Tau fluvalinate	22.52	250.06	181.06	206.00
Alachlor	13.22	160.11	188.11	146.10	Nitrofen	16.52	202.02	282.98	139.05	Fenvalerato	22.68	225.08	125.02	167.06
Tolclofos-methyl	13.25	264.98	124.98	249.96	Chloropropylate	16.65	138.99	251.00	253.00	Difenoconazole	23.04	264.98	323.02	202.02
Metalaxyl	13.34	160.11	206.12	132.08	Dicofol, 4,4	16.65	138.99	251.00	215.03	Indoxacarb	23.14	203.02	218.04	235.05
Fenclorfos	13.44	284.93	124.98	269.91	Endrin	16.66	262.86	242.95	280.93	Deltametrin	23.43	181.06	252.90	171.99
Spiroxamine	13.44	100.11	126.13	198.15	Carbophenothion methyl	16.7	156.95	124.98	142.97	Azoxistrobin	23.63	344.10	329.08	388.09
Heptachlor	13.48	271.81	236.84	100.01	Diniconazole	16.78	268.00	270.00	232.03	Dimethomoph	23.87	301.06	165.05	303.06
Prometryn	13.52	184.07	226.11	199.09	Oxadixyl	16.8	132.08	163.10	233.09	Imazalil				
Pirimiphos-methyl	13.59	290.07	276.06	180.11	Etion	16.82	230.97	202.94	124.98					
S421 (Octachlorodipropyl ether)	13.59	129.91	180.11	82.95	DDD-o,p (Mitotane)	16.87	235.01	165.07	176.06					

Have questions or want more details on implementing this method? We would love to help!
*Visit **www.phenomenex.com/Chat** to get in touch with one of our Technical Specialists*

Figure 1. Profile of 268 Pesticides on a Zebron™ ZB-5MS*PLUS*™ GC Column.



Results and Discussion

Pesticide analysis is extremely challenging due to the number of pesticide compounds that one might be looking for. **Table 1** shows the 268 pesticides included in the developed method with their retention times and the three main ions obtained in high resolution scan mode. All the compounds were monitored by three characteristic ions that provide adequate selectivity for their determination. High resolution applied for obtaining such ions ensure a drastic diminution of interferences and elimination of matrix effect. It reduces significantly the risk of false positive or negative results. All the compounds were registered in the software for automatic detection of the compounds in target mode. The highest intensity ion is used for quantification of the compounds by monitoring the extracted ion chromatogram. Chromatographic peaks were quantified by peak area relative to the one of the internal standards. The other two ions were used for confirming the results. Mass accuracy resulted very useful for increasing reliability of the results. In **Figure 1**, a total ion chromatogram obtained with the proposed experimental conditions is shown for an apple extract spiked at a concentration level of 0.500 mg/kg.

Calibration was performed using three replicates of each calibration point. The working range for every compound was calculated and considered a linear calibration because it is the most typical calibration function selected in routine laboratories. **Figure 2** shows an example of the linearity with the results of the pesticide Atrazine. All the proposed working ranges generated a R^2 higher or equal to 0.99 and adequate recoveries for all the studied concentrations (**Table 2**). An example of the chromatographic peaks obtained while monitoring the quantification ion of one of the studied pesticides for the calibration curve can be seen in **Figure 3**. This shows the stability of the retention time for the pesticide.

The recovery and precision of the method have been calculated at 0.01 and 0.1 mg/kg (n=5). Recoveries were considered as acceptable when they were between 70 and 120 %. Precision was expressed as relative standard deviation (%RSD) (**Table 3**).

Over 200 real samples were analyzed to evaluate the robustness of the chromatographic method and stationary phase on the Zebron ZB-5MS*PLUS* GC column. Different fruits and vegetables were tested. A selection of matrices were used here as an example including oranges, lemons, and bananas, to detect trace levels of pesticides in them (**Figure 4-6**).

Figure 2. Calibration curve obtained for the pesticide Atrazine. Working range between 0.001 and 0.250 mg/kg.

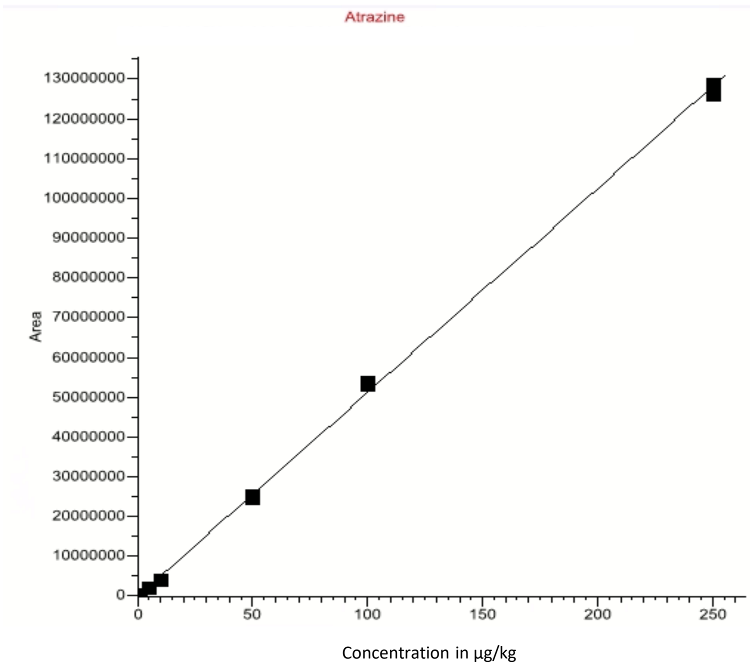


Table 2. Calibration Curve R^2 Values for Pesticides

Compound Name	R^2	Compound Name	R^2	Compound Name	R^2
1,4-Dimetilnaftaleno	0.998942219	Cyfluthrin	0.998741963	Fenpropimorph	0.999120732
2-phenylphenol	0.998386807	Cypermethrin	0.997370526	Fenson	0.997326316
3,5-Dichloroaniline (3,5-Dichlorobenzenamine)	0.998630422	Cyproconazole	0.998974836	Fenthion	0.999217523
4,4-Dibromobenzophenone	0.998386517	Cyprodinil	0.999115342	Fenvalerate	0.998299334
4,4-Diclorobenzofenon	0.998228884	Chinomethionate	0.998256561	Fipronil	0.99877209
4-Chloro-3-methylphenol	0.996688092	Chlordane (CIS)	0.998506236	Fipronil sulfone	0.998210819
Aclonifen	0.99353018	Chlorflurenol-methyl	0.999313753	Flucythrinate	0.998086264
Acrinathrin	0.998209792	Chloropropylate	0.997820634	Fluchloralin	0.994865125
Alachlor	0.999028669	Chlorothalonil	0.999210031	Fludioxonil	0.99906409
Aldrin/Aldrin-r	0.998418941	Chlorpyrifos – ethyl	0.998568648	Flumetralin	0.999314275
Anthraquinone	0.998542205	Chlorpyrifos – methyl	0.999224693	Flumioxazin	0.993295923
Atrazine	0.999238283	DCPA (Clortal dimetil)	0.998981624	Fluotrimazole	0.998048853
Azoxystrobin	0.99829505	DDD-o,p (Mitotane)	0.998890375	Fluquinconazol	0.99941145
Benalaxyl	0.998976646	Deltamethrin	0.997991024	Fluvalinate (Tau)	0.994672664
Benfluralin	0.995444223	Diazinone	0.998518326	Fonofos	0.999106042
Benfuresate	0.998892031	Diclofop-methyl	0.998777327	Formothion	0.999287337
Benodalil	0.998558157	Dicofol, 4,4	0.998832171	Furalaxyl	0.99916366
Benoxacor	0.99725214	Dichlobenil (Benzonitrile, 2,6-dichloro-)	0.99907646	Halfenprox	0.990197591
Benzene, hexachloro	0.999296242	Dichlofenthion	0.998759718	Heptacloro-epoxido-A-endo (cis)	0.998631709
Benzyl benzoate	0.997957247	Dichloran (Botran)	0.99916187	Heptacloro-epoxido-B-exo (trans)	0.99819743
Bifenazato	0.97333699	Dichlorvos	0.998739233	Heptachlor	0.999479566
Biphenyl	0.998079986	Dieldrin	0.998706712	Heptenophos	0.998630245
Bifenox	0.999503797	Difenoconazole	0.998548285	Hexachlorocychlohexane-alfa	0.999450172
Bifenthrin	0.998892937	Diflufenican	0.998751621	Hexaconazole	0.999224733
Bitertanol	0.996683478	Dimethomoph	0.996333623	Hexazinone	0.998034805
Boscalid	0.998999274	Diniconazole	0.999205997	Indoxacarb	0.997968095
Bromacil	0.9988172	Diphenylamine	0.998483731	Iodofenphos	0.999332257
Bromocyclen	0.998985819	Disulfoton	0.99793204	Iprodione	0.997695069
Bromophos-ethyl	0.999045465	Ditalimfos	0.998949092	Isobenzan	0.998425394
Bromophos-methyl	0.999417057	Edifenphos	0.998653756	Isocarbophos	0.99880613
Bromopropylate	0.99904998	Endosulfan ether	0.998638926	Isodrin	0.998901603
Bupirimate	0.998402377	Endosulfan sulfate	0.999399315	Isofenphos	0.99858637
Buprofezin	0.998783956	Endrin	0.998706712	Isofenphos-methyl	0.998971183
Butafenacil	0.995907777	Endrin ketone	0.999094107	Isomethiozin	0.999269117
Butilate	0.997556098	EPTC (Eptam)	0.999078096	Isopropalin	0.999300247
Butralin	0.99961669	Esfenvalerate	0.998456522	Isoprothiolane	0.998929638
Cadusafos	0.998957049	Ethion	0.991168804	Kresoxim-methyl	0.998635139
Carbophenothion	0.998919631	Ethoprophos	0.999075798	Lambda Cyhalothrin	0.999275047
Carbophenothion methyl	0.987212444	Ethoxyquin	0.99138868	Lenacile	0.998788016
Cinidon-ethyl	0.995907777	Etridiazole	0.999002176	Leptophos	0.998874746
CIS 1,2,3,6-Tetra-hydrophthalimide	0.995423132	Etrimfos	0.999232783	Lindane-gamma	0.999450172
Clodinafop-propargyl	0.993635698	Famfur (Fonofos)	0.999047473	Malathion	0.996880777
Chlorfenapyr	0.999057548	Fenamiphos	0.998265698	Mefenpyr-diethyl	0.997472144
Chlorfenprop methyl	0.998813165	Fenamiphos sulfone	0.99780723	Mepanipyrim	0.998854165
Chlorfenson /Ovex	0.999135823	Fenamiphos sulfoxide	0.999045189	Metalaxyl	0.998927861
Chlorfenvinphos	0.999093123	Fenarimol	0.998445175	Metazachlor	0.999315932
Chlormephos	0.998383875	Fenazaquin	0.995167663	Methamidophos	0.991286302
Chlorpropham	0.998562723	Fenbuconazol	0.998503846	Methidation	0.998985109
Clortion	0.975372542	Fenchlorphos/Ronnel	0.99932361	Methoxychlor	0.995563934
Chlozolinate	0.998486175	Fenhexamid	0.991202336	Metolachlor	0.998984445
Crimidine	0.998782904	Fenitrothion	0.999177411	Mevinphos	0.998805054
Cyanofenphos	0.998919631	Fenobucarb	0.999194468	Mirex	0.999450884
Cyanophos	0.998731622	Fenoxaprop-P-ethyl	0.998502038	Myclobutanil	0.998623477
Cycloate	0.999135817	Fenoxycarb	0.998782417		
Cyflufenamid	0.999161703	Fenpropathrin	0.998961115		

Have questions or want more details on implementing this method? We would love to help!
*Visit **www.phenomenex.com/Chat** to get in touch with one of our Technical Specialists*

Figure 3. Chromatographic peaks obtained monitoring the quantification ion of the pesticide bromophos-ethyl.

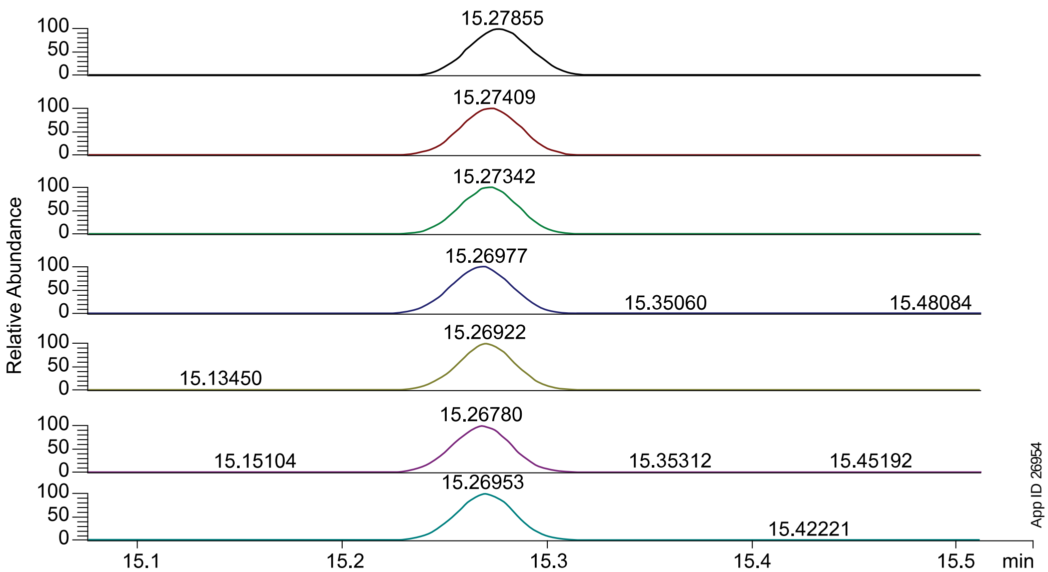


Table 3. Recovery and Precision for Pesticides on a Zebron™ ZB-5MS*PLUS*™ GC Column.

Compound Name	10 µg/kg		100 µg/kg		Compound Name	10 µg/kg		100 µg/kg		Compound Name	10 µg/kg		100 µg/kg	
	%Recovery	%RSD	%Recovery	%RSD		%Recovery	%RSD	%Recovery	%RSD		%Recovery	%RSD	%Recovery	%RSD
1,4-Dimetilnaftaleno	87.4	10.2	90.3	12.3	Cyfluthrin	104.8	11.8	98.7	10.2	Fenpropimorph	95.4	13.8	103.2	14.3
2-phenylphenol	90.3	9.6	93.1	8.8	Cypermethrin	96.3	10.4	93.2	8.3	Fenson	87.3	17.1	88.3	14.3
3,5-Dichloroaniline (3,5-Dichlorobenzenamine)	79.4	15.3	85.3	10.1	Cyproconazole	79.3	8.9	89.3	8.2	Fenthion	81.7	15.7	90.8	13.5
4,4-Dibromobenzophenone	91.8	16.3	94.1	12.4	Cyprodinil	89.6	13.4	103.4	10.3	Fenvalerate	95.6	14.8	102.5	10.6
4,4-Diclorobenzofenon	88.5	13.9	90.4	8.6	Chinomethionate	79.3	15.6	93.2	11.0	Fipronil	97.1	18.8	110.2	16.9
4-Chloro-3-methylphenol	103.7	9.3	97.6	7.3	Chlordane (CIS)	96.1	16.3	92.3	13.2	Fipronil sulfone	104.6	8.6	89.3	10.3
Aclonifen	90.7	11.4	97.5	6.8	Chlorflurenol-methyl	89.6	11.3	92.2	8.7	Flucythrinate	101.5	18.0	95,6	17.3
Acrinathrin	96.8	13.7	96.1	8.8	Chloropropylate	109.2	7.9	101.2	6.0	Fluchloralin	67.4	12.4	81.2	9.9
Alachlor	76.6	17.9	79.9	15.8	Chlorothalonil	103.7	16.7	87.3	12.4	Fludioxonil	78.7	9.6	90.0	6.9
Aldrin/Aldrin-r	79.0	16.8	80.4	10.3	Chlorpyrifos – ethyl	96.3	15.8	97.3	11.2	Flumetralin	84.2	11.9	93.2	10.2
Anthraquinone	87.4	12.6	89.5	10.7	Chlorpyrifos – methyl	90.4	19.2	94.6	16.9	Flumioxazin	93.2	12.3	96.5	13.9
Atrazine	90.7	9.4	92.3	9.0	DCPA (Clortal dimetil)	88.2	12.4	93.2	10.2	Fluotrimazole	78.4	7.9	79.3	6.8
Azoxystrobin	103.9	10.3	90.5	6.6	DDD-o,p (Mitotane)	80.5	15.7	94.5	13.8	Fluquinconazol	84.3	11.0	93.1	7.9
Benalaxyl	99.0	14.3	94.8	10.0	Deltamethrin	79.6	17.3	78.4	13.5	Fluvalinate (Tau)	81.9	15.3	87.8	11.6
Benfluralin	78.5	17.3	79.9	14.6	Diazinone	96.4	14.2	89.5	9.0	Fonofos	90.5	19.8	89.3	17.4
Benfuresate	73.3	16.3	79.0	10.4	Diclofop-methyl	80.9	19.4	86.7	15.6	Formothion	92.3	17.8	100.2	14.2
Benodalil	98.7	12.6	96.9	9.5	Dicofol, 4,4	79.4	16.6	98.5	16.9	Furalaxyl	106.4	12.6	98.3	9.8
Benoxacor	103.8	16.2	100.4	9.0	Dichlobenil (Benzonitrile, 2,6-dichloro-)	81.5	21.2	85.6	17.8	Halfenprox	94.6	10.7	90.3	12.2
Benzene, hexachloro	78.9	15.7	79.0	13.7	Dichlofenthion	76.3	18.3	86.5	13.4	Heptacloro-epoxido-A-endo (cis)	92.8	14.7	87.5	11.8
Benzyl benzoate	86.4	12.3	96.9	8.9	Dichloran (Botran)	87.5	16.2	83.2	12.9	Heptacloro-epoxido-B-exo (trans)	94.1	15.3	97.4	12.4
Bifenazato	88.0	10.2	97.2	6.4	Dichlorvos	85.3	14.7	93.4	9.6	Heptachlor	83.2	10.6	89.5	11.3
Biphenyl	98.7	8.7	96.4	8.0	Dieldrin	106.8	12.1	98.2	9.6	Heptenophos	79.4	9.7	86.9	8.9
Bifenox	88.9	11.3	90.9	7.4	Difenoconazole	98.8	11.9	89.4	7.8	Hexachlorocychlohexane-alfa	75.2	15.6	84.3	13.4
Bifenthrin	94.3	9.4	98.5	4.8	Diflufenican	86.1	9.7	96.7	6.4	Hexaconazole	56.6	13.2	80.3	9.7
Bitertanol	103.5	11.0	97.5	7.0	Dimethomoph	85.7	8.6	91.2	5.7	Hexazinone	88.6	18.4	98.3	16.9
Boscalid	89.4	12.8	90.9	10.1	Diniconazole	96.6	16.5	99.3	11.7	Indoxacarb	78.7	17.3	79.3	15.1
Bromacil	97.0	6.0	101.3	5.4	Diphenylamine	78.5	14.9	89.3	13.4	Iodofenphos	106.5	11.7	89.3	9.0
Bromocyclen	93.1	11.6	87.6	8.3	Disulfoton	94.2	17.4	94.5	12.4	Iprodione	112.4	9.4	102.2	7.9
Bromophos-ethyl	90.7	16.3	98.7	11.2	Ditalimfos	89.1	15.7	97.4	11.3	Isobenzan	89.6	10.6	87.3	6.0
Bromophos-methyl	101.5	12.1	89.5	9.6	Edifenphos	80.4	6.8	88.2	6.0	Isocarbophos	78.5	10.0	83.2	9.7
Bromopropylate	87.6	7.9	95.3	6.8	Endosulfan ether	95.3	19.0	105.4	16.9	Isodrin	81.9	8.9	87.6	6.9
Bupirimate	90.4	13.2	91.2	10.9	Endosulfan sulfate	93.7	17.7	89.4	16.4	Isofenphos	96.4	12.3	94.3	10.8
Buprofezin	79.0	8.9	89.2	9.0	Endrin	109.3	16.8	101.2	10.9	Isofenphos-methyl	104.5	15.9	97.9	15.4
Butafenacil	102.4	14.5	97.3	111.2	Endrin ketone	105.3	18.2	97.5	14.5	Isomethiozin	97.8	17.2	95.4	11.8
Butilate	108.5	17.3	87.3	16.8	EPTC (Eptam)	98.3	15.4	103.2	12.8	Isopropalin	60.5	7.6	73.4	7.0
Butralin	98.3	16.1	89.3	13.2	Esfenvalerate	91.1	11.0	93.4	8.5	Isoprothiolane	88.4	12.8	89.8	13.2
Cadusafos	87.5	20.0	94.5	16.6	Ethion	100.2	8.9	96.4	6.0	Kresoxim-methyl	79.0	9.9	90.0	9.0
Carbophenothion	90.8	18.3	98.5	14.2	Ethoprophos	107.3	10.7	98.5	8.6	Lambda Cyhalothrin	80.9	11.2	88.4	8.9
Carbophenothion methyl	90.2	6.9	97.4	5.9	Ethoxyquin	78.4	12.3	85.7	10.0	Lenacile	103.5	14.9	89.3	11.7
Cinidon-ethyl	76.1	10.9	79.4	8.5	Etridiazole	83.4	14.6	91.4	12.7	Leptophos	86.4	17.4	85.3	15.6
CIS 1,2,3,6-Tetra-hydrophthalimide	85.9	13.6	89.3	10.2	Etrimfos	79.8	18.0	85.0	13.4	Lindane-gamma	97.9	22.8	98.4	18.9
Clodinafop-propargyl	97.4	15.4	89.4	10.2	Famfur (Fonofos)	90.1	17.3	99.5	14.5	Malathion	73.2	16.8	75.5	11.1
Chlorfenapyr	98.0	9.4	87.6	7.4	Fenamiphos	80.0	15.8	84.6	9.9	Mefenpyr-diethyl	78.3	11.9	92.2	9.0
Chlorfenprop methyl	68.9	11.3	78.8	6.9	Fenamiphos sulfone	89.4	14.2	97.4	9.7	Mepanipyrim	106.6	9.0	97.3	6.9
Chlorfenson /Ovex	88.9	17.5	90.0	12.3	Fenamiphos sulfoxide	70.4	16.3	79.5	11.4	Metalaxyl	89.5	15.3	87.4	13.4
Chlorfenvinphos	79.6	17.1	94.3	13.2	Fenarimol	79.2	13.7	84.3	7.9	Metazachlor	98.7	17.2	104.5	14.9
Chlormephos	70.2	13.4	83.4	9.8	Fenazaquin	84.5	14.1	89.3	9.0	Methamidophos	76.4	12.7	79.5	8.9
Chlorpropham	89.9	9.7	88.5	6.9	Fenbuconazol	87.2	23.2	100.3	17.9	Methidation	97.3	10.7	96.5	7.9
Clortion	88.5	22.3	98.8	17.3	Fenchlorphos/Ronnel	79.2	18.3	87.4	15.3	Methoxychlor	87.6	15.6	94.3	11.9
Chlozolinate	90.9	18.4	94.5	12.7	Fenhexamid	103.2	16.5	97.1	11.3	Metolachlor	95.2	17.2	99.3	17.9
Crimidine	66.5	16.9	75.6	13.2	Fenitrothion	77.6	17.2	87.4	12.6	Mevinphos	91.9	8.9	94.3	7.6
Cyanofenphos	87.3	8.5	102.3	8.0	Fenobucarb	86.2	11.3	98.5	8.9	Mirex	78.3	16.0	83.2	14.3
Cyanophos	97.4	14.3	106.3	11.7	Fenoxaprop-P-ethyl	79.0	7.8	87.4	5.8	Myclobutanil	79.4	14.9	86.4	11.8
Cycloate	79.3	17.4	86.3	12.3	Fenoxycarb	103.2	13.2	98.3	13.4					
Cyflufenamid	90.9	16.8	95.4	15.7	Fenpropathrin	107.4	8.4	95.4	8.9					

Figure 4. Orange sample containing 0.016 mg/kg of pyrimethanil.

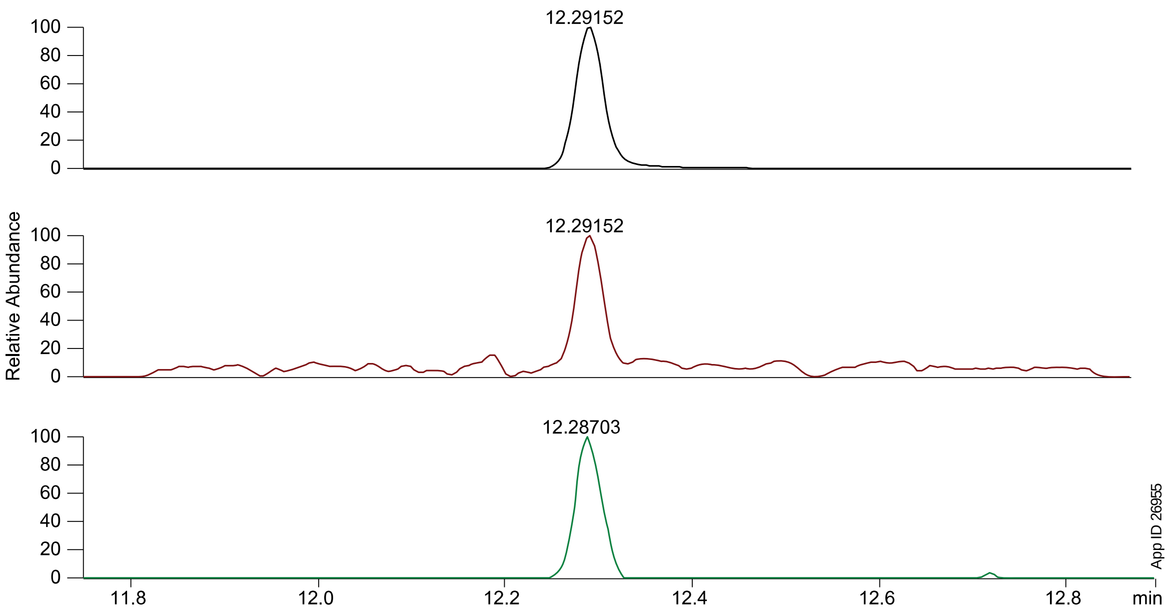


Figure 5. Lemon sample containing 0.023 mg/kg of pyriproxifen.

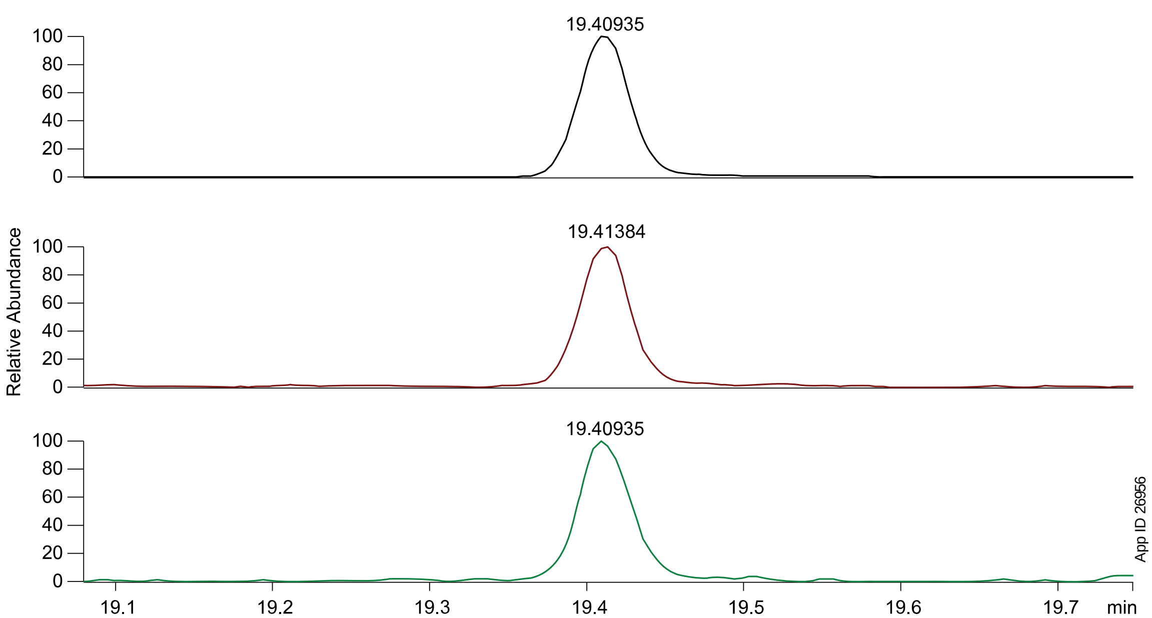
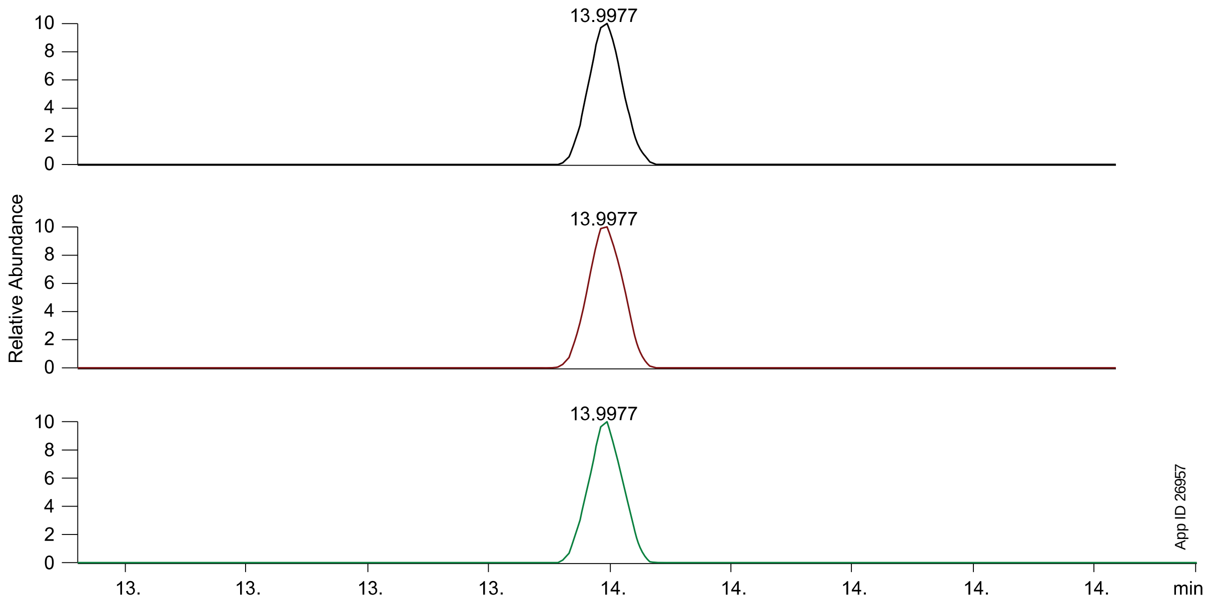


Figure 6. Banana sample containing 0.016 mg/kg of pyrimethanil.



Conclusions

The application presented in this tech note demonstrates detection and recovery of 268 multi-pesticide compounds from various fruit matrices. In addition, the method is linear over a wide range to accommodate trace level detection of pesticides from real samples. The Zebron™ ZB-5MS*PLUS*™ GC column not only gave adequate separation and inertness, but also provided reproducible retention with multiple injections of real samples and proving the robustness of the stationary phase.

Ordering Information

Zebron™ ZB-5MS*PLUS*™ GC Columns

ID(mm)	df(µm)	Temp. Limits °C	Part No.
1.5-Meter			
0.25	0.25	-60 to 325/350	7XG-G030-11
15-Meter			
0.25	0.25	-60 to 325/350	7EG-G030-11
0.25	0.50	-60 to 325/350	7EG-G030-17
0.25	1.00	-60 to 325/350	7EG-G030-22
20-Meter			
0.18	0.18	-60 to 325/350	7FD-G030-08
0.18	0.36	-60 to 325/350	7FD-G030-53
30-Meter			
0.25	0.25	-60 to 325/350	7HG-G030-11
0.25	0.50	-60 to 325/350	7HG-G030-17
0.25	1.00	-60 to 325/350	7HG-G030-22
0.32	0.25	-60 to 325/350	7HM-G030-11
0.32	0.50	-60 to 325/350	7HM-G030-17
0.32	1.00	-60 to 325/350	7HM-G030-22
0.32	1.50	-60 to 325/350	7HM-G030-28
0.53	1.00	-60 to 325/350	7HK-G030-22
0.53	3.00	-60 to 325/350	7HG-G030-36
30-Meter with 5-Meter Guardian™ Integrated Guard			
0.25	0.25	-60 to 325/350	7HG-G030-11-GGA
0.25	0.50	-60 to 325/350	7HG-G030-17-GGA
30-Meter with 5-Meter Guardian™ Integrated Guard			
0.25	0.25	-60 to 325/350	7HG-G030-11-GGC
0.25	0.50	-60 to 325/350	7HG-G030-17-GGC
60-Meter			
0.25	0.25	-60 to 325/350	7KG-G030-11
0.25	1.00	-60 to 325/350	7KG-G030-22
0.32	1.00	-60 to 325/350	7KM-G030-22

Note: If you need a 5 in. cage, contact Technical support via Phenomenex.com/chat or simply reach out to your Technical consultant. Conditions may apply. Agilent 6850, some SRI and process GC systems use only 5 in. cages.

roQ™ Extraction Kits

Description	Unit	Part No.
AOAC 2007.01 Method Extraction Kits		
6.0 g $MgSO_4$, 1.5 g NaOAc	50/pk	KS0-8911*
EN 15662 Method Extraction Kits		
4.0 g $MgSO_4$, 1.0 g NaCl, 1.0 g SCTD, 0.5 g SCDS	50/pk	KS0-8909*
Original Non-Buffered Method Extraction Kits		
4.0 g $MgSO_4$, 1.0 g NaCl	50/pk	KS0-8910
6.0 g $MgSO_4$, 1.5 g NaCl	50/pk	KS0-8912

*AOAC and EN Extraction Kits also available in traditional non-collared 50 mL centrifuge tubes, Part No.: KS0-8911-NC and KS0-8909-NC

Need a different column size or sample preparation format?

No problem! We have a majority of our available dimensions up on www.phenomenex.com, but if you can't find what you need right away, our super helpful Technical Specialists can guide you to the solution via our online chat portal www.phenomenex.com/Chat.

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