Application Note

Instrument: Pegasus® BT 4D

Determination of Pesticides in Tomato by GCxGC-TOFMS

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Key Words: Pesticides, Food, GCxGC, TOFMS, Qualitative and Quantitative Analysis

Introduction

The tomato is the second most important vegetable crop next to potato. Global tomato production is currently around 130 million tons. The top 5 largest tomato producers are: China, EU, India, USA, and Turkey. They account for 70% of global production. Most of the fresh tomatoes are immediately processed into products such as juice, puree and paste, ketchup/sauce, or canned whole. The presence of pesticide residues in such products can cause a number of adverse health effects. Therefore, the identification and quantitation of pesticides is an important task in the context of food control authorities.

This note describes a GCxGC-TOFMS workflow for the detection and quantitation of targeted pesticides in peeled tomatoes. The need for a comprehensive two-dimensional chromatographic method has been dictated by the huge amount of matrix interferences encountered in the sample, even after a traditional QuEChERS extraction followed by a clean-up step. In fact, the GCxGC technology significantly increases the separation efficiency, and ultimately allows a better separation of the target and non-target analytes from the matrix interferences. This, in combination with LECO's Pegasus® BT 4D sensitivity, fast acquisition and deconvolution benefits, allowed to easily reach the required limit of detections for all the pesticides investigated.

Experimental

A peeled tomato extract was obtained employing a QuEChERS extraction according to the European EN 15662 (Restek #25849) followed by a dSPE clean-up step (Restek # 26223) on a 10 g sample provided by a customer. The blank extract has been initially analyzed to confirm the absence of any pesticide contamination and then used for the preparation of the matrix-matched quantitation standards. A concentrated standard mix of 164 pesticide residues was provided by the same customer. This has been used to spike the blank matrix of peeled tomato for the preparation of the calibration standards at different levels (2.5, 5, 10, 25, and 50 ng/g).

The data for matrix-matched standards were collected using the conditions reported in Table 1 and processed in ChromaTOF® brand software using the NonTarget Deconvolution® (NTD®) along with the peak find algorithm and the Target Analyte Finding (TAF) strategy to identify and quantify incurred pesticides and non-target substances.

Peak detection, identification, and linearity of the calibration curves followed the SANTE/11813/2017 guidelines for unit mass resolution TOFMS (http://www.eurl-pesticides.eu/docs/public/tmplt_article.asp?CntID=727), as already described in LECO's App Note 203-821-560.

Table 1. *Pegasus* BT 4D GCxGC Conditions

GC	**LECO GCxGC QuadJet™ Thermal Modulator**
Injection	1 µL, in cold Splitless mode (Gerstel CIS4 Inlet) 40 °C (hold 6s), 10 °/s to 275 °C Splitless time: 2 min
Columns	1D: HP-5MS UI, 30 m x 0.25 mm i.d. x 0.25 µm coating (Agilent) 2D: Rxi-17Silms, 1.5 m x 0.15 mm ID x 0.15 µm coating (Restek)
Oven Program	75 °C (hold 2.05 min), ramp 5 °C/min to 320 °C (hold 15 min)
Secondary Oven	+5 °C (relative to the main oven temperature)
Modulator	+15 °C (relative to the secondary oven temperature)
Modulation Period	4 sec (0-862 s), 5s (862-end of run)
Transfer line	340 °C
MS	**LECO *Pegasus* BT 4D**
Ion Source Temp	250 °C
Mass Range	40-600
Acquisition Rate	200 spectra/s

Results and Discussion

Figure 1 shows a two-dimensional contour plot from the 50 ng/g spiked peeled tomato extract. In addition to the 164 spiked pesticides, more than 2100 non-target peaks with a spectral similarity score higher than 800/1000 (i.e. 80 %) were identified. This show the capability of the *Pegasus* BT 4D to perform non target screening whilst collecting data to be used for trace level quantitative purposes. Moreover, these data can be used at a later stage for retrospective analysis in case of new regulated pesticide substances and/or for different evaluations such as the determination of Volatile Organic Compounds (VOCs) responsible of tomato flavor and aroma.

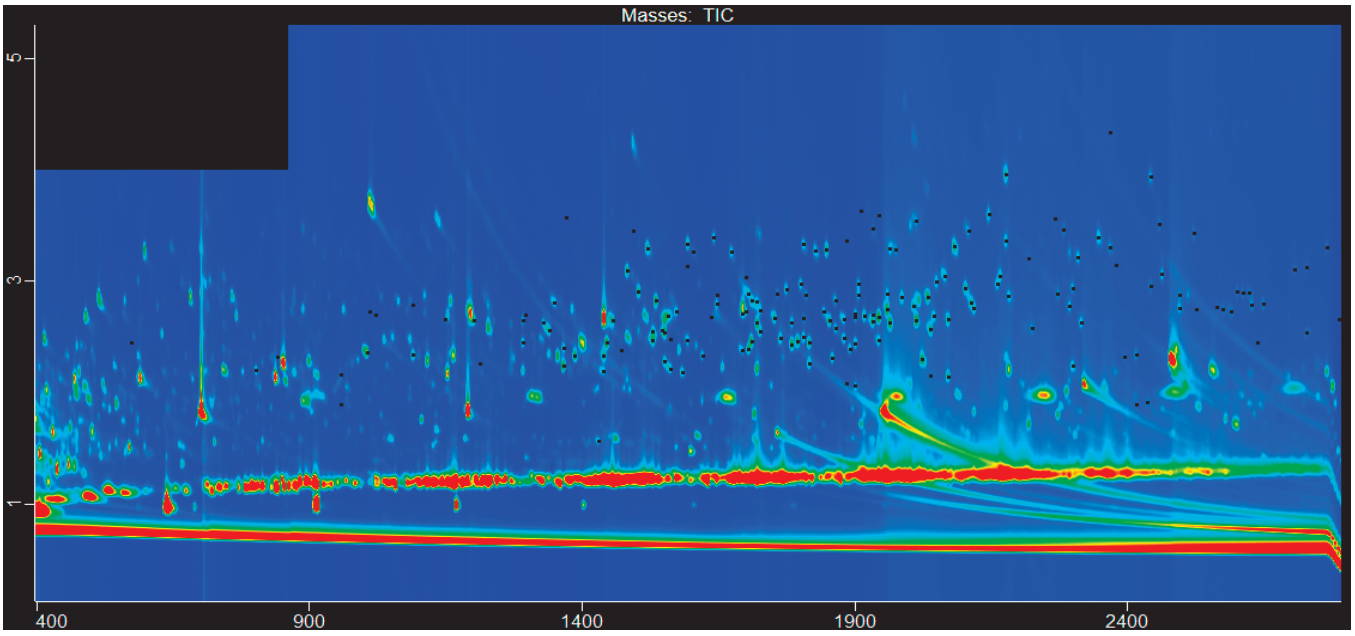

Figure 1. Contour Plot of a peeled tomato extract spiked with 50 ng/g pesticide mix.

The 2D contour plot in Figure 1 also illustrates the application of the variable modulation period at the beginning of the run, in order to preserve the 1D chromatographic resolution for early eluting target peaks. In particular, between 0 and ~860 sec, the modulation period has been set to 4 sec, whilst it was extend to 5 sec until the end of the run, to increase the separation capabilities of the method, avoiding at the same time any wrap-around for late eluting compounds.

An example of the enhanced resolving power of the GCxGC technology is shown in Figure 1a, which highlights the chromatographic separation on the "y" axis of the contour plot. In fact, in a one-dimensional separation, the three pesticides δ -Lindane, Paraoxon methyl, and Disulfoton would coelute, whilst they are completely resolved thanks to the 2nd dimension column separation. Moreover, within the same picture, an example of automatic deconvolution is shown, between Pirimicarb and Pantachloroaniline.

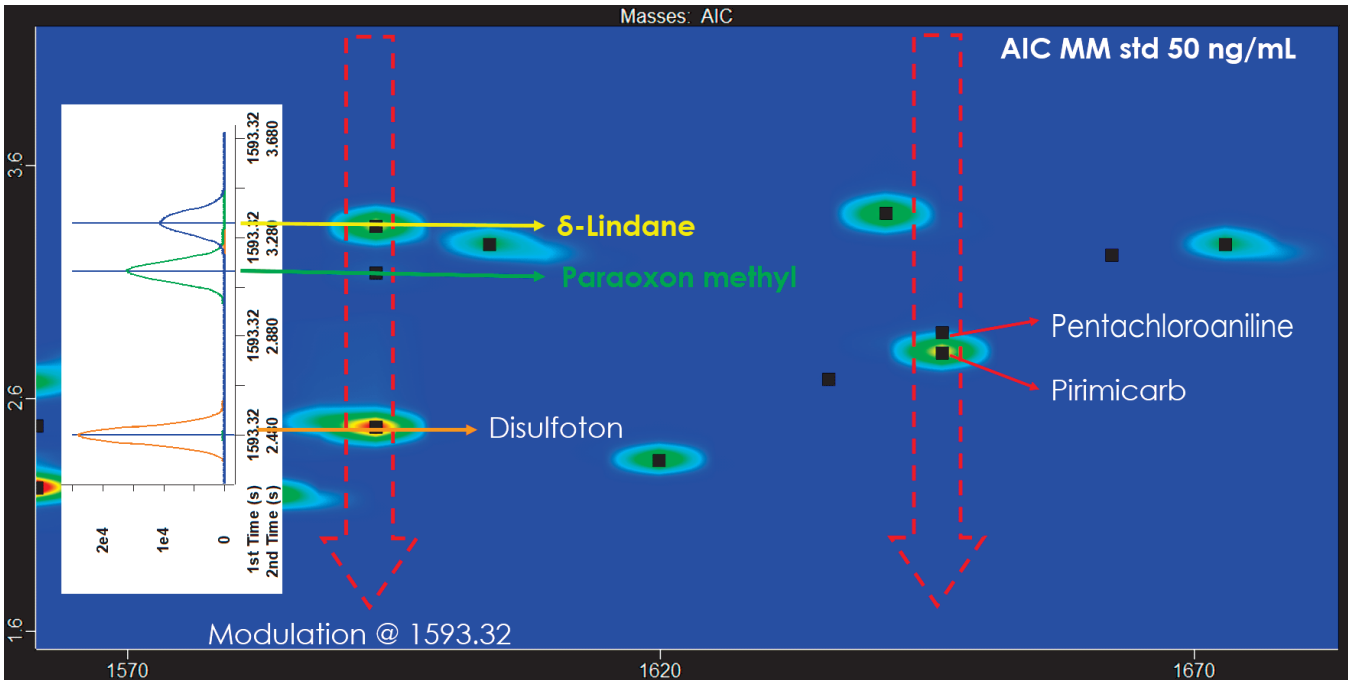

Figure 1a. Examples of the enhanced resolving power of GCxGC and deconvolution benefits.

Calibration and quantification with TOFMS are similar to what would be performed in a selected ion recording experiment with quadrupole or magnetic sector mass spectrometers. In addition to that, LECO's *Pegasus* BT 4D TOFMS always provides full m/z range data, which can be processed using NTD peak find mode or TAF strategy for quantitative purposes.

In this note, all the target pesticides were quantitated using matrix-matched external standard calibration approach with the hexachlorobenzene used as internal standard, resulting in linear calibration curves with great correlation coefficients (R^2) as shown in Figure 2 for Chlorothalonil, a synthetic fungicide that controls both early blight and late blight, and Fenitrothion, an organophosphate insecticide widely used worldwide.

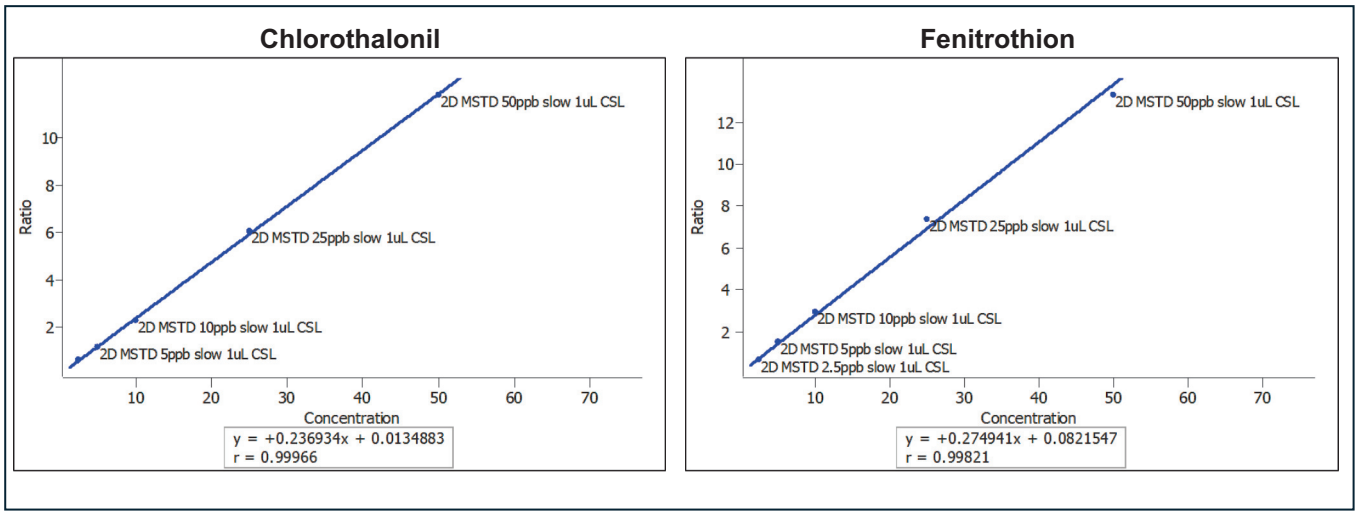

Figure 2. Calibration curves for Chlorothalonil and Fenitrothion.

Ion ratios have been also calculated to assess their stability throughout the calibration range. An example is showed in Figure 3 for Cyanazine and Dicofol, two of the regulated pesticides in tomato. The calculation has been completely done within the *ChromaTOF* environment, leading to an easy to evaluate goodness of the calibration.

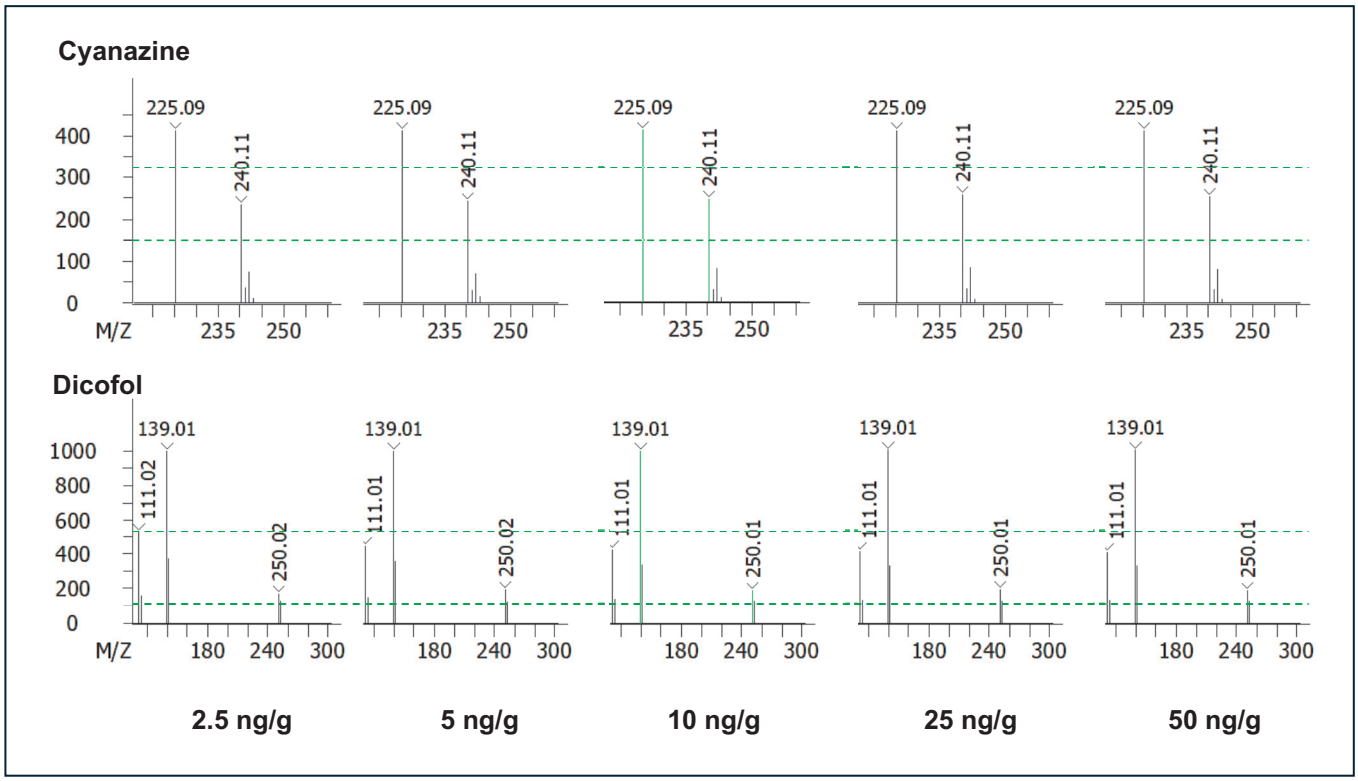

Figure 3. Ion Ratio variability (<±30%) across the calibration range.

As mentioned at the beginning of the section, LECO's *Pegasus* BT 4D can be used for both non-target and target screening at the same time without compromising the required level of sensitivity needed for pesticide's analysis. As an example of non-target screening, Figure 4 shows the identification of three aroma-active substances found in the extract, namely 5-Hepten-2-one, 6-methyl-, methyl salicylate, and beta-ionone. The first is responsible for a green-leafy aroma, the second for a green, minty one, and the third for a floral, violet. The non-target substances have been identified with high Similarity Score values, respectively 932, 888, and 859 out of 1000 and were nicely separated from matrix interferences in the two-dimensional space.

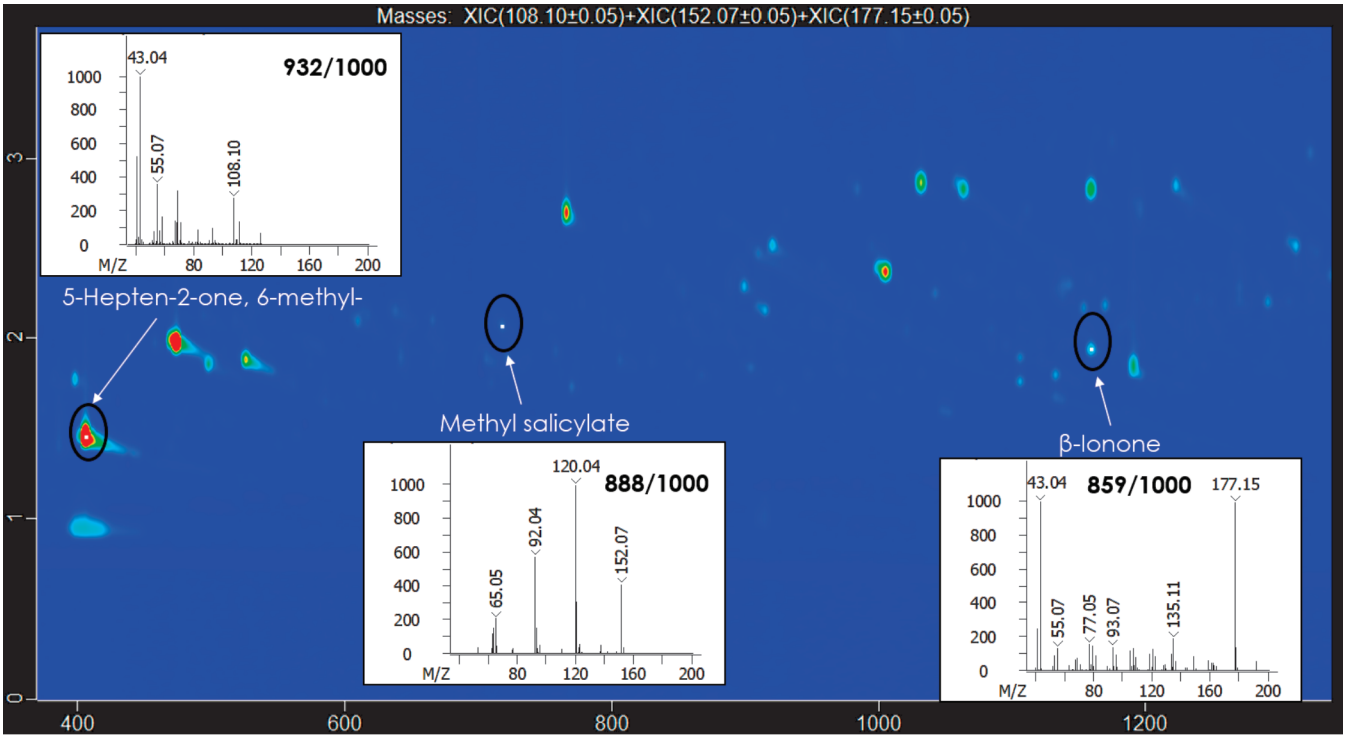

Figure 4. Results of the non-target screening for aroma-active substances.

Figure 4a shows the 2D separation between beta-Ionone and Apocynin, two compounds having the same 1D R.T. and very close Retention Indices (RI) according to the NIST library information (respectively 1491 and 1489). In consideration of this, the two components wouldn't have been separated in a conventional 1D separation and therefore, their precise identification might have been affected. Moreover, also the sensory perception of the beta-Ionone could have been impacted, in the case of experiments made for the assessment of the aroma-active components (e.g. GC-Olfactometry).

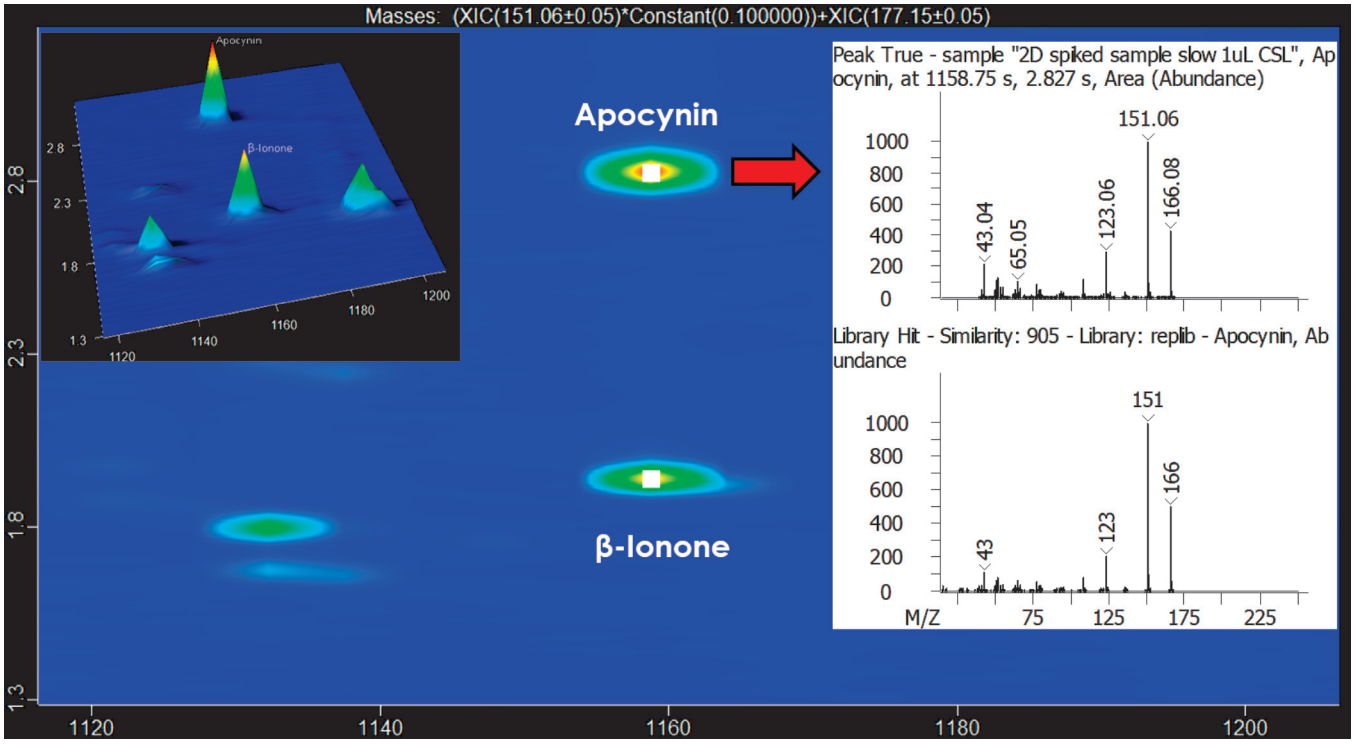

Figure 4a. Detail of the 2-dimensional separation between beta-Ionone and Apocynin.

Table 2 (see page 6 & 7) displays the list of pesticides along with their two-dimensional Retention Times, sub-nominal m/z ions used for quantification (Quant Masses), signal-to-noise levels (Quant S/N) at the lowest calibrated level (i.e. 2.5 ng/g), and the corresponding Maximum Residue Levels (MRLs) in tomato. As can be seen from the table, all the pesticides have been calibrated in a range sufficiently below the MRLs set for tomato. Moreover, the calculated Quant S/N provides interesting information about the LODs and LOQs attainable for most of the target components. In fact, in many cases, it would be possible to reach LODs value as low as 0.5 to 1 ng/g and even lower by modifying the injection volume to 2 μL. This was, anyway, out of the scope of this application.

Conclusions

GCxGC-TOF MS: Comprehensive two-dimensional gas chromatography (GCxGC) improved the overall separation of all individual target pesticides from coelutions deriving from either another pesticide or the matrix components.

Quantitation: A quantitation workflow has been developed for the determination of a target list of pesticides in peeled tomato extract by means of the LECO's *Pegasus* BT 4D system (GCxGC-TOFMS). All the target pesticides have been correctly calibrated using an external calibration curve approach employing Matrix- Matched standards with linear calibration curves with great correlation coefficients (R^2).

Sensitivity: From a sensitivity point of view, the instrumental methodology has proven to be able to quantify down to low ppb levels (i.e. 2.5 ppb) with 1μL cold splitless injection. Moreover, based on the S/N calculated at the lowest calibration level, there is still a huge potential to detect and quantify target pesticides at lower levels (0.5-1 ng/g).

Non-Target Screening: GCxGC-TOFMS technology has been successfully employed to simultaneously detect and identify non-target components (i.e. aroma-active substances) using the same data set, mainly used for quantitative purposes. This demonstrates the flexibility of such an instrument and technology which proved to be very helpful in a modern analytical laboratory.

Acknowledgements

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Table 2 - Pesticide List

#	Name	Eu MRL in tomato (ng/g)	Quant Masses	1st Dim. R.T.(s)	2nd Dim. R.T. (s)	Quant S/N (2.5 ng/g)
1	Dichlorvos	10	XIC(109.01±0.1)	801.971	2.21	428
2	Biphenyl	10	XIC(154.08±0.1)	1005.06	2.38	2551
3	Mevinphos	10	XIC(127.03±0.1)	1079.25	2.80	150
4	Chlormephos	-	XIC(96.96±0.1)	1089.85	2.35	445
5	Dicrotophos	-	XIC(96.96±0.1)	1089.85	2.35	257
6	Propham	10	XIC(179.09±0.1)	1116.35	2.29	463
7	o-Phenylphenol	10	XIC(170.09±0.1)	1201.15	2.67	467
8	Molinate	10	XIC(126.1±0.1)	1227.64	2.58	407
9	DEET	-	XIC(119.06±0.1)	1291.24	2.47	325
10	Heptenophos	-	XIC(250.02±0.1)	1291.24	2.67	207
11	Tecnazene	10	XIC(260.87±0.1)	1328.34	2.49	391
12	Thionazin	-	XIC(248.04±0.1)	1328.34	2.64	123
13	Propachlor	20	XIC(120.08±0.1)	1338.94	2.58	510
14	Diphenylamine	50	XIC(169.09±0.1)	1349.54	2.82	775
15	Ethoprophos	20	XIC(242.06±0.1)	1365.43	2.43	186
16	Cycloate	-	XIC(83.09±0.1)	1365.43	2.26	536
17	Chlorpropham	10	XIC(213.06±0.1)	1386.63	2.35	639
18	Trifluralin	10	XIC(335.11±0.1)	1429.03	1.58	1075
19	Cadusafos	10	XIC(158.98±0.1)	1439.63	2.22	120
20	Sulfotep	-	XIC(322.02±0.1)	1439.63	2.35	341
21	Phorate	10	XIC(260.01±0.1)	1444.93	2.47	350
22	alpha-Lindane	10	XIC(180.96±0.1)	1455.53	2.67	471
23	Dicloran	10	XIC(205.96±0.1)	1482.03	3.10	200
24	Chlorzoxazone	-	XIC(169.01±0.1)	1492.63	3.47	34
25	Simazine	10	XIC(201.08±0.1)	1503.23	2.93	277
26	Beta-Lindane	10	XIC(180.96±0.1)	1519.13	3.31	436
27	Atrazine	50	XIC(215.09±0.1)	1519.13	2.69	368
28	Propazine	-	XIC(229.11±0.1)	1529.72	2.49	685
29	Terbumeton	-	XIC(225.16±0.1)	1529.72	2.55	344
30	gamma-Lindane	10	XIC(180.96±0.1)	1535.02	2.84	524
31	Quintozene	20	XIC(294.83±0.1)	1545.62	2.58	219
32	Terbufos	10	XIC(230.99±0.1)	1550.92	2.29	173
33	Terbuthylazine	50	XIC(229.11±0.1)	1550.92	2.56	730
34	Fonofos	-	XIC(246.03±0.1)	1556.22	2.71	667
35	Propyzamide	10	XIC(255.02±0.1)	1561.52	2.23	695
36	Pyrimethanil	1000	XIC(199.11±0.1)	1572.12	2.75	666
37	Diazinon	10	XIC(137.09±0.1)	1582.72	2.21	220
38	Delta-Lindane	10	XIC(180.96±0.1)	1593.32	3.35	247
39	Disulfoton	10	XIC(186.01±0.1)	1593.32	2.49	116
40	Paraoxon methyl	10a	XIC(230.04±0.1)	1593.32	3.15	32
41	Chlorothalonil	6000	XIC(265.9±0.1)	1603.92	3.28	136
42	Tefluthrine	-	XIC(177.05±0.1)	1609.22	1.62	330
43	Etrimphos	-	XIC(292.06±0.1)	1619.82	2.36	188
44	Endosulfan ether	50	XIC(341.85±0.1)	1635.72	2.70	4
45	Formothion	10	XIC(93.02±0.1)	1641.02	3.41	238
46	Pirimicarb	500	XIC(238.14±0.1)	1646.32	2.83	433
47	Metribuzin	100	XIC(198.09±0.1)	1672.82	3.24	244
48	Vinclozoline	10	XIC(285.02±0.2)	1694.01	2.40	112
49	Chloropyriphos-methyl	1000	XIC(285.95±0.1)	1694.01	2.71	364
50	Malaoxon	20	XIC(127.04±0.1)	1699.31	2.75	410
51	Simetryn	-	XIC(213.12±0.1)	1699.31	3.05	16*
52	Heptachlor	10	XIC(100.02±0.1)	1704.61	2.41	428
53	Tolclofos-methyl	10	XIC(265.01±0.1)	1704.61	2.91	290
54	Parathion methyl	10a	XIC(125±0.1)	1704.61	2.90	174
55	Alachlor	10	XIC(160.13±0.1)	1709.91	2.48	487
56	Ametryn	-	XIC(227.14±0.1)	1709.91	2.84	456
57	Paraoxon-ethyl	-	XIC(275.06±0.1)	1720.51	2.83	64
58	Prometryn	-	XIC(241.14±0.1)	1720.51	2.64	570
59	Fenchlorphos	10	XIC(284.95±0.1)	1725.81	2.56	532
60	Metalaxyl	300	XIC(279.15±0.1)	1725.81	2.76	151
61	Terbutryn	-	XIC(241.14±0.1)	1752.31	2.70	655
62	Fenitrothion	10	XIC(277.02±0.1)	1757.61	2.91	120
63	Pirimiphos methyl	10	XIC(305.1±0.1)	1762.91	2.51	318
64	Dichlofluanid	-	XIC(331.96±0.1)	1773.51	2.94	317
65	Aldrin	10	XIC(66.06±0.1)	1784.11	2.44	290
66	Malathion	20	XIC(127.05±0.1)	1784.11	2.64	245
67	Metolachlor	50	XIC(162.14±0.1)	1794.71	2.48	793
68	Fenthion	10	XIC(278.02±0.1)	1800.01	2.99	252
69	Chlorpyrifos-ethyl	-	XIC(350.92±0.1)	1805.31	2.51	377
70	Cyanazine	-	XIC(240.09±0.1)	1805.31	3.34	227
71	Parathion ethyl	-	XIC(291.03±0.1)	1805.31	2.68	65
72	Dicofol	20	XIC(139.01±0.1)	1810.61	2.90	234
73	Chlorthal-dimethyl	10	XIC(300.9±0.1)	1815.91	2.46	3359
74	Flufenacet	50	XIC(363.07±0.1)	1815.91	2.28	278
75	Fenson	-	XIC(77.05±0.1)	1826.51	3.29	308
76	Bromophos-methyl	-	XIC(330.9±0.1)	1842.4	2.75	275
77	Diphenamid	-	XIC(72.05±0.1)	1847.7	3.30	732
78	Isodrin	-	XIC(192.95±0.1)	1853	2.66	144
79	Pirimiphos ethyl	-	XIC(333.13±0.1)	1858.3	2.33	221
80	Cyprodinil	1500	XIC(224.14±0.1)	1863.6	2.85	302
81	Isofenphos-methyl	-	XIC(199.03±0.1)	1863.6	2.59	240
82	Heptachlor epoxide	10	XIC(387.81±0.1)	1879.5	2.67	428
83	Pendimethalin	50	XIC(252.12±0.1)	1879.5	2.50	332
84	Fipronil sulfide	-	XIC(350.98±0.1)	1884.8	2.09	11
85	Chlozolinate	10	XIC(331.02±0.1)	1890.1	2.41	398
86	Fipronil	5	XIC(366.97±0.1)	1900.7	2.08	261
87	Chlorfenvinphos	10	XIC(323.02±0.1)	1900.7	2.70	73
88	Mecarbam	10	XIC(329.05±0.1)	1900.7	2.73	106
89	Isofenphos	-	XIC(255.1±0.1)	1900.7	2.47	216
90	Quinalphos	10	XIC(298.05±0.1)	1906	2.89	191
91	Phenthoate	-	XIC(274.01±0.1)	1906	2.99	135
92	Folpet	5000	XIC(104.04±0.1)	1911.3	3.64	36*
93	Procymidone	10	XIC(283.02±0.1)	1916.6	2.71	98
94	Methidathion	20	XIC(145.02±0.1)	1932.5	3.47	115
95	Chlordane-trans	-	XIC(372.85±0.1)	1932.5	2.65	1383
96	Bromophos-ethyl	10	XIC(96.96±0.1)	1943.1	2.49	182
97	o,p'-DDE	-	XIC(317.93±0.1)	1943.1	2.70	698
98	Tetrachlorvinphos	-	XIC(328.96±0.1)	1959	2.97	271
99	alpha-Endosulfan	50b	XIC(194.97±0.1)	1959	2.77	252
100	Chlordane-cis	10	XIC(372.85±0.1)	1964.3	2.65	292
101	Mepanipyrim	1500	XIC(223.11±0.1)	1964.3	3.36	404
102	Ditalimfos	-	XIC(299.04±0.1)	1974.9	3.31	98
103	Fenamiphos	40	XIC(303.11±0.1)	1985.5	2.86	203
104	Profenofos	10000	XIC(373.93±0.1)	2006.69	2.81	154
105	Fludioxonil	3000	XIC(248.06±0.1)	2011.99	3.56	208
106	p,p'-DDE	50c	XIC(317.93±0.1)	2011.99	2.66	606
107	Oxadiazon	50	XIC(344.07±0.1)	2022.59	2.31	367
108	o,p'-DDD	-	XIC(235.03±0.1)	2033.19	2.87	792
109	Buprofezin	10	XIC(305.16±0.1)	2038.49	2.58	144
110	Bupirimate	2000	XIC(316.16±0.1)	2043.79	2.69	68
111	Kresoxim-methyl	600	XIC(116.06±0.1)	2049.09	3.01	204
112	Endrin	10	XIC(262.88±0.1)	2064.99	3.05	118
113	Perthane	-	XIC(223.17±0.1)	2070.29	2.68	620
114	Fluazifop-butyl	60d	XIC(383.13±0.1)	2070.29	2.17	232
115	Beta-Endosulfan	50b	XIC(194.97±0.1)	2080.89	3.32	162
116	Aclonifen	10	XIC(264.05±0.1)	2107.39	3.47	319
117	o,p'-DDT	50	XIC(235.03±0.1)	2112.69	2.82	699
118	p,p'-DDD	-	XIC(235.03±0.1)	2112.69	2.82	695
119	Ethion	10	XIC(96.96±0.1)	2117.99	2.78	305
120	Triazophos	10	XIC(313.06±0.1)	2144.49	3.63	160
121	Carbofenotion	-	XIC(341.97±0.1)	2160.38	3.00	128
122	Benalaxyl	500	XIC(148.13±0.1)	2165.68	3.07	255
123	Lenacil	100	XIC(153.08±0.1)	2176.28	3.99	548
124	Endosulfan sulphate	50b	XIC(421.81±0.1)	2176.28	3.38	476
125	p,p'-DDT	50c	XIC(235.03±0.1)	2181.58	2.88	270
126	Methoxychlor I	10	XIC(227.13±0.1)	2218.68	3.22	53
127	Propargite	10	XIC(350.15±0.1)	2223.98	2.60	37
128	Iprodione	10	XIC(329.03±0.1)	2271.68	2.90	114
129	Pyridaphenthion	-	XIC(340.06±0.1)	2282.28	3.48	57
130	Tetramethrin I	-	XIC(164.09±0.1)	2287.58	3.00	29
131	Bromopropylate	10	XIC(340.92±0.1)	2292.88	2.79	275
132	Bifenthrin	300	XIC(181.12±0.1)	2298.18	2.27	274
133	Tetramethrin II	-	XIC(164.09±0.1)	2298.18	2.97	152
134	Methoxychlor II	10	XIC(227.13±0.1)	2308.77	3.23	328

Table 2 - Pesticide List, continued

#	Name	Eu MRL in tomato (ng/g)	Quant Masses	1st Dim. R.T.(s)	2nd Dim. R.T. (s)	Quant S/N (2.5 ng/g)
135	Fenpropathrin	10	XIC(97.11±0.1)	2314.07	2.65	103
136	Tetradifon	10	XIC(355.88±0.1)	2345.87	3.40	376
137	Phosalone	10	XIC(366.99±0.1)	2367.07	3.32	31*
138	Azinphos-methyl	50	XIC(77.05±0.1)	2367.07	4.34	48
139	.lambda.-Cyhalothrin I	70e	XIC(181.09±0.1)	2393.57	2.34	48
140	Acrinathrin I	20	XIC(181.09±0.1)	2414.77	1.92	31*
141	.lambda.-Cyhalothrin II	70e	XIC(181.09±0.1)	2414.77	2.36	57
142	Acrinathrin II	20	XIC(181.09±0.1)	2435.97	1.93	55
143	Pyrazophos	10	XIC(221.1±0.1)	2441.27	2.98	84
144	Azinphos-ethyl	20	XIC(77.05±0.1)	2441.27	3.96	102
145	Dialiphos	-	XIC(208.04±0.1)	2457.17	3.53	48
146	Fenoxaprop-ethyl	-	XIC(361.07±0.1)	2462.46	3.09	89
147	Spirodiclofen	500	XIC(71.09±0.1)	2494.26	2.76	86
148	Permethrin cis	50f	XIC(183.1±0.1)	2494.26	2.88	87
149	Permethrin trans	50f	XIC(183.1±0.1)	2494.26	2.89	10
150	Coumaphos	-	XIC(96.96±0.1)	2520.76	3.45	51
151	Cyfluthrin I	50f	XIC(163.03±0.1)	2563.16	2.79	27
152	Cyfluthrin II	50f	XIC(163.03±0.1)	2573.76	2.77	55
153	Cyfluthrin III	50f	XIC(163.03±0.1)	2589.66	2.75	76
154	Cypermethrin I	500f	XIC(163.03±0.1)	2600.26	2.93	43
155	Cypermethrin III	500f	XIC(163.03±0.1)	2621.45	2.93	49
156	Flucythrinate I	10f	XIC(199.12±0.1)	2626.75	2.81	154
157	Fluvalinate I	-	XIC(250.08±0.1)	2637.35	2.47	13
158	Cypermethrin II	500f	XIC(163.03±0.1)	2637.35	2.47	58
159	Flucythrinate II	10f	XIC(199.12±0.1)	2647.95	2.82	64
160	Fenvalerate I	-	XIC(419.13±0.1)	2706.25	3.12	84
161	Fenvalerate II	-	XIC(419.13±0.1)	2727.45	3.15	68
162	Fluvalinate II	-	XIC(250.08±0.1)	2727.45	2.56	76
163	Deltamethrin I	70f	XIC(181.09±0.1)	2764.55	3.32	40
164	Deltamethrin II	70f	XIC(181.09±0.1)	2785.74	2.68	39

**Calculated on the 5 ng/mL standard*
a (sum of Parathion-methyl and paraoxon-methyl expressed as Parathion-methyl)
b (sum of alpha- and beta-isomers and endosulfan-sulphate expresses as endosulfan)
c (sum of p,p´-DDT, o,p´-DDT, p-p´-DDE and p,p´-TDE (DDD) expressed as DDT)
d (sum of all the constituent isomers of fluazifop, its esters and its conjugates, expressed as fluazifop)
e (includes gamma-cyhalothrin) (sum of R,S and S,R isomers)
f (sum of isomers)