Determination of 287 Pesticides at Trace Levels by GCxGC–TOFMS

Sjaak de Koning, Monika Gumpendobler • LECO Instrumente, Mönchengladbach, Germany

Key Words: GCxGC, TOFMS, Pesticides, Trace Analysis, Quantification, Food

1. Introduction

The determination of trace contaminants in complex matrixes, such as food, often requires extensive sample extraction and preparation regimes prior to instrumental analysis. In recent years, the use of mass spectrometry in instrumental analysis has enabled the 'extraction' of an analyte at the detection stage of a method. This has led to the development of crude extractions—due to the need for rapid and universal methods, covering a large number of compounds down to the levels required by legislation [1,2]. For example, the QuEChERS method for pesticides analysis [3], which is based on dispersive solid phase extraction (DSPE), uses lower volumes of solvent and little or no clean-up.

The purpose of this study is the evaluation of a GCxGC-TOFMS method for the trace analysis of pesticides in food stuffs.

2. Instruments and Methods

LECO Pegasus® 4D GCxGC–TOFMS

GC Conditions

Column 1: 30 m x 0.25 mm x 0.2 µm Rtx-CLPesticides II
Column 2: 1.1 m x 0.1 mm x 0.1 mm Rxi-17

Inlet: CIS4 PTV (GERSTEL)

Rate (°C/min)	Target Temp (°C)	Duration (min)
Initial	40	0.25
720	280	8.00

Primary Oven

Rate (°C/min)	Target Temp (°C)	Duration (min)
Initial	95	5.00
10	200	0.00
7	270	0.00
10	320	10.00

Secondary Oven

Rate (°C/min)	Target Temp (°C)	Duration (min)
Initial	105	6.00
10	360	15.00

Modulator Offset: +30°C from the primary oven
Modulation Period: 5 seconds (0.6 seconds hot pulse)
Injection: 2 µl, CTC CombiPAL
Carrier Gas: He, 26 psi constant pressure
Transfer Line: 250°C

TOFMS Conditions

Mass Range: 50 to 600 amu
Acquisition Rate: 200 spectra/second
Source: 200°C

3. Results

After analysis of all the analytical standards (n=7) for all pesticides in the range of 0.1 to 1000 pg/µl, the retention time was determined from the 250 pg/µL standard (see Figure 1 for TIC surface plot). This standard was used as the reference standard for further work. For all pesticides the analytical data as determined are shown in Table 1.

As seen by viewing the second dimension of the GCxGC contour plot in Figure 1, many coelutions would occur when analyzing in a single dimension mode. Figure 2 displays a zoomed section of the contour plot indicating the coelution of four pesticides along the second dimension. However, these four pesticides are separated due to the selectivity of the second orthogonal separation. Although the peak capacity and resolving power of GCxGC is very high, coelutions can still occur. Figure 3 shows an example of how the True Signal Deconvolution™ algorithm in ChromaTOF® software can be used to identify coeluting peaks, delivering true peak spectra.

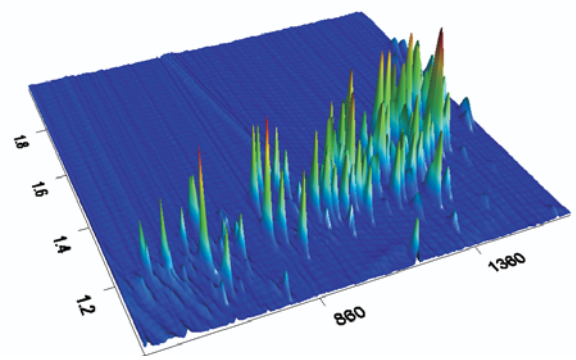

Figure 1: TIC surface plot showing all pesticides studied.

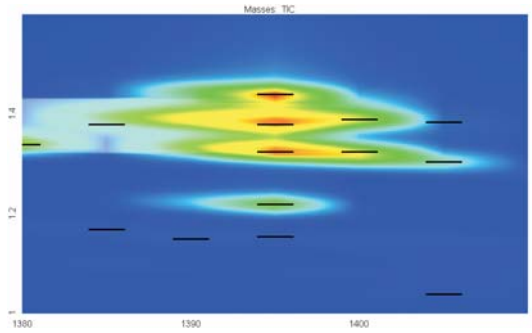

Figure 2: Zoomed contour plot indicating coelution in the first dimension, but separation in the second dimension.

Life Science and Chemical Analysis Solutions

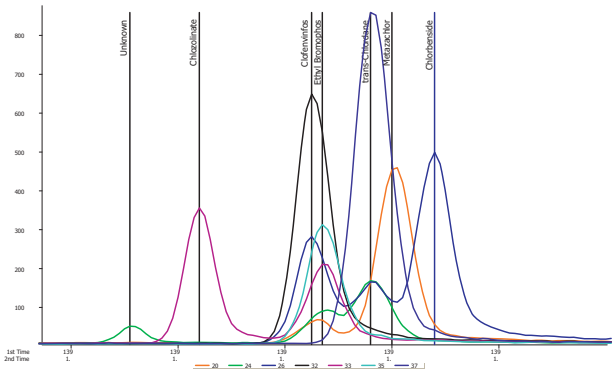

Figure 3: Zoomed EIC of coeluting compounds. Peak identifications are displayed at the peak markers.

4. Conclusions

It has been shown that the LECO Pegasus 4D GCxGC–TOFMS equipped with a GERSTEL CIS4 PTV injector is able to analyze hundreds of pesticides in a single run. The use of GCxGC provides an enhanced separation mechanism that helps eliminate coelutions and provides users a very structured and visually stimulating chromatogram.

5. References

[1] Commision Directive 2003/13/EC, *Off. J. Eur. Com.* L41 (2003) 33.

[2] Commision Directive 2003/14/EC, *Off. J. Eur. Com.* L41 (2003) 37.

[3] M. Anastassiades, S.J. Lehotay, D. Stajnbaher, F.J. Schenk, *J. AOAC Int.* 86 (2003) 412.

Table 1. Pesticides analytical data.

Analyte	Compound Name	LOD* (pg/µl)	Quant Mass	1st Dim. R.T. (s)	2nd Dim. R.T. (s)
1	Aniline	0.55	93	385	1.285
2	o-Cresol	0.20	108	435	1.245
3	m-Cresol	0.17	108	455	1.245
4	m-Cresol	0.63	107	460	1.205
5	Methomyl	12.65	105	475	1.245
6	Dimefox	0.72	154	505	1.060
7	Propoxur	1.78	110	595	1.115
8	Aniline, 2,6-dimethyl-	0.26	121	600	1.245
9	Aniline, 2,5-dimethyl-	0.51	106	610	1.175
10	Aniline, 3-chloro-	0.09	127	645	1.295
11	Aniline, 4-chloro-	0.79	127	665	1.235
12	Bendiocarb	0.54	151	690	1.205
13	Dichlorphos	0.37	185	715	1.115
14	Metamidophos	13.80	141	730	1.280
15	Eptc	0.22	128	770	1.100
16	Dichlobenil	0.11	171	825	1.205
17	3,5-Dichloroaniline	0.13	161	840	1.310
18	Vernolate	0.06	128	845	1.110
19	Chlormephos	0.33	234	865	1.200
20	a-HCH	1.82	181	875	1.235
21	Etridiazol	0.61	183	875	1.245
22	3,4-Dichloroaniline	0.09	161	875	1.340
23	Propham	1.13	137	880	1.180
24	Mevinphos cis	0.23	127	895	1.145
25	Mevinphos trans	6.89	127	905	1.180
26	Benzene, pentachloro-	0.19	250	915	1.250
27	Methacrifos	2.36	180	920	1.205
28	o-Hydroxybiphenyl	0.37	170	925	1.330
29	Acephate	1.91	136	935	1.275
30	Phenol, 2,3,4,5-tetrachloro-	1.52	232	945	1.315
31	Tebuthiuron	1.35	156	970	1.280
32	Crimidine	0.26	142	975	1.275
33	Oxamyl	15.52	145	990	1.330
34	Propyzamide	7.32	240	995	1.160
35	Chlorfenprop-methyl	0.96	196	995	1.240
36	Demeton-o	2.42	171	1005	1.195
37	Heptenophos	2.44	124	1005	1.265
38	Cycloate	0.14	154	1010	1.240
39	b-HCH	2.32	289	1010	1.300
40	Tecnazen	0.49	261	1015	1.250
41	Diphenylamine	0.19	169	1020	1.375
42	Thionazin	0.98	143	1025	1.270
43	Tributyl phosphate	0.14	155	1030	1.075
44	Ethoprophos	1.29	200	1030	1.220
45	Chloropropham	1.72	213	1035	1.215
46	Propachlor	1.46	176	1040	1.235
47	Trifluralin	0.37	306	1045	0.970
48	Chlordimeform	2.15	181	1045	1.255
49	Diallate	0.54	234	1050	1.220
50	Demeton-S-methyl	2.99	142	1050	1.275
51	Fluometuron	2.78	232	1060	1.155
52	Tridemorph	2.87	128	1065	1.035
53	Benzene, hexachloro-	0.38	284	1070	1.310
54	Sulfotep	1.16	322	1075	1.215
55	Diallate:2	4.43	234	1075	1.225
56	Pentachloroanisole	0.55	237	1075	1.305
57	Phorate	0.33	121	1080	1.270
58	Omethoat	1.11	156	1080	1.340
59	ETU	1.43	102	1085	1.565
60	Lindane	0.52	183	1090	1.300
61	Bendiocarb	0.81	151	1090	1.355
62	Ethoxyquine	1.96	202	1100	1.265
63	Thiometon	0.51	125	1100	1.320
64	Chlorbufam	1.03	223	1115	1.270
65	Demeton-s	1.17	170	1120	1.240
66	Dicrotophos	1.27	127	1125	1.265
67	Simazine	2.62	201	1125	1.335
68	Terbufos	0.67	231	1130	1.225
69	Atrazine	0.37	200	1130	1.280
70	Propyzamide	0.26	173	1135	1.180
71	Propazine	1.51	214	1135	1.240
72	Monocrotophos	4.30	127	1135	1.290
73	Diazinone	2.39	304	1140	1.215
74	Triethazine	0.37	200	1140	1.270
75	Quintozene	0.99	237	1140	1.290
76	Dichloran	0.40	176	1145	1.325
77	Propetamphos	0.36	194	1150	1.210
78	Terbuthylazine	9.50	214	1150	1.275
79	Fonofos	0.29	137	1150	1.335
80	Pyrimethanil	0.23	198	1150	1.365
81	Triallate	0.68	268	1155	1.240
82	g-HCH	0.76	181	1155	1.340
83	Carbofuran	1.62	164	1155	1.365
84	Cyromazine	0.68	151	1155	1.565
85	Carbofuran	2.07	164	1160	1.380
86	Fluchloralin	0.52	306	1165	1.015
87	Dioxothion	5.97	270	1165	1.350
88	Disulfaton	0.97	186	1170	1.280
89	Dimethoate	14.59	125	1170	1.370
90	Benazolin	20.21	170	1170	1.435
91	Aziprotryne	16.69	166	1175	1.310
92	Dimethoate	0.51	125	1175	1.385
93	Cyanophos	0.58	243	1195	1.270
94	Azolamide	0.22	142	1200	1.405
95	Pentachloroaniline	0.28	265	1205	1.415
96	Dichlofenthion	0.62	279	1210	1.250
97	Dazomet	4.19	162	1210	1.480
98	y-HCH	1.37	181	1215	1.370
99	Desmethryn	0.53	213	1220	1.390
100	Pirimicarb	0.46	166	1225	1.330
101	Heptachlor	1.37	272	1225	1.345
102	Terbacil	2.34	161	1225	1.360
103	Metobromuron	1.18	172	1230	1.305
104	Ethiofencarb	2.45	168	1240	1.385
105	Dimethipin	1.16	118	1240	1.445
106	Vinclozoline	1.82	285	1245	1.205
107	Methylparaoxon	3.91	230	1245	1.265
108	Methyl chlorpyrifos	0.33	286	1245	1.350
109	Metribuzin	0.48	198	1245	1.420
110	Dimethachlor	1.14	197	1250	1.280
111	Fenchlorphos	0.87	285	1255	1.325
112	Ametryn	0.36	227	1255	1.360
113	Tolclofos methyl	1.46	265	1255	1.370
114	Dodemorph	0.84	154	1260	1.220
115	Alachlor	1.04	188	1260	1.260
116	Formothion	4.26	170	1265	1.340
117	Pirimiphos methyl	1.02	290	1270	1.305
118	Aldrin	0.58	263	1275	1.365
119	Pentanochlor	0.29	141	1280	1.235

Analyte	Compound Name	LOD* (pg/µl)	Quant Mass	1st Dim. R.T. (s)	2nd Dim. R.T. (s)
120	Metalaxyl	1.06	206	1280	1.295
121	Fuberidazole	0.80	184	1280	1.485
122	Phosphamidon (isomer)	1.28	127	1285	1.245
123	Methyl parathion	0.62	263	1285	1.300
124	Carbaryl	2.44	144	1290	1.435
125	Dodemorph	0.34	154	1295	1.230
126	Telodrin	1.40	311	1300	1.325
127	Thiobencarb	1.29	257	1300	1.355
128	Methiocarb	11.96	168	1305	0.855
129	Linuron	8.31	160	1305	1.305
130	Paraoxon	2.98	109	1310	1.215
131	Metolachlor	1.58	238	1310	1.265
132	Chlorpyriphos	0.15	197	1310	1.300
133	Trichloronat	2.22	269	1315	1.290
134	Nitrothale-isopropyl	2.52	194	1320	1.090
135	Ethofumesate	1.03	161	1320	1.280
136	Phenitrothion	2.25	277	1320	1.310
137	Triadimefon	0.98	208	1325	1.235
138	Fenthion	0.73	278	1325	1.400
139	Pirimiphos ethyl	1.02	318	1330	1.280
140	4,4'-Dichlorobenzophenone	0.19	139	1330	1.350
141	Isodrine	0.33	193	1330	1.405
142	Bromazil	1.14	205	1335	1.415
143	Butralin	0.47	266	1340	1.160
144	Anthraquinone	0.45	180	1345	1.470
145	Parathion	1.11	291	1350	1.250
146	Oxychlordan	8.67	185	1350	1.355
147	Allethrin	1.10	123	1355	1.165
148	Carbetamide	6.13	119	1355	1.310
149	Bioallethrin	1.31	123	1360	1.170
150	Crufomate	0.85	256	1360	1.310
151	Heptachlor epoxide	0.99	353	1365	1.375
152	Penoxaline	0.84	252	1370	1.260
153	trans-Chlorfenvinphos	3.36	267	1370	1.280
154	Isofenphos	0.46	213	1375	1.285
155	Penconazole	3.51	159	1375	1.295
156	Demeton-S-methyl sulfone	3.73	169	1375	1.360
157	Cyanazine	1.45	225	1380	1.340
158	Fensone	0.16	141	1380	1.395
159	o,p'-DDE	0.19	246	1385	1.415
160	Triadimenol	0.90	168	1390	1.270
161	Bromophos-ethyl	0.23	303	1390	1.325
162	Chlozolinate	0.64	188	1395	1.220
163	Clofenvinfos	0.61	267	1395	1.325
164	Chlorbromuron	1.72	294	1395	1.355
165	Quinalphos	2.28	298	1395	1.375
166	trans-Chlordane	1.37	373	1395	1.380
167	Chlorbenside	0.74	268	1395	1.440
168	Triflumizole	1.81	206	1400	1.170
169	Triadimenol	0.71	168	1400	1.280
170	Ethyl Bromophos	1.72	303	1400	1.325
171	Metazachlor	1.73	133	1400	1.390
172	Phenthoate	0.95	274	1400	1.410
173	Mecarbam	2.16	159	1405	1.305
174	Crotoxyphos	1.39	127	1415	1.325
175	Furalaxyl	2.65	242	1415	1.410
176	Endosulfan I	4.00	356	1415	1.460
177	Procymidone	0.71	283	1420	1.290
178	Chinomethionate	0.37	234	1420	1.490
179	Thiabendazole	3.46	201	1420	1.625
180	Paclobutrazide	1.06	236	1430	1.305
181	Prothiophos	0.91	162	1440	1.360
182	Tetrachlorvinphos	0.65	329	1440	1.375
183	p,p-DDE	0.32	246	1440	1.400
184	Folpet	25.14	260	1445	1.510
185	Allethrin	4.69	123	1450	1.205
186	Diethatyl ethyl	1.15	188	1450	1.305
187	trans-Chlorfenvinphos	0.25	267	1455	1.370
188	Iodofenfos	0.91	377	1455	1.480
189	Methidathion	0.35	145	1455	1.490
190	Fenamiphos	2.45	303	1460	1.350
191	o,p'-DDD	0.37	235	1465	1.445
192	Buprofezine	0.62	172	1470	1.375
193	Dieldrin	1.15	263	1470	1.440
194	Ditalimfos	0.36	130	1470	1.455
195	Enilconazole	4.82	215	1475	1.335
196	Barban	4.08	222	1475	1.470
197	Fluazifop-butyl	0.59	282	1480	1.215
198	Chlorfenson	0.26	175	1480	1.415
199	Diclobutrazole	1.03	270	1490	1.335
200	Fluzilazol	0.69	233	1495	1.325
201	Chloropropylate	0.72	251	1495	1.345
202	Buprimate	3.30	316	1495	1.360
203	Jasmoline I	22.56	123	1500	1.220
204	Chlorthiophos I	1.88	222	1500	1.400
205	Vamidothion	2.08	145	1500	1.470
206	Chlorthiophos II	17.65	222	1505	1.410
207	Chlorobenzilate	0.28	251	1510	1.390
208	Dinapacryl	35.78	83	1515	1.230
209	Chlorthiophos III	11.91	269	1515	1.420
210	Endrin	1.76	263	1515	1.518
211	Myclobutanil	0.89	179	1520	1.340
212	p,p'-TDE	0.15	235	1520	1.460
213	Tetrasul	0.44	252	1520	1.485
214	o,p-ddt	1.21	235	1520	1.495
215	Nitrofen	1.28	283	1525	1.420
216	Flufenprop-isopropyl	0.16	105	1530	1.340
217	p,p-DDD	1.22	235	1530	1.455
218	Chlorodecone	7.65	272	1535	1.520
219	Ethion	1.19	231	1540	1.430
220	Chlorthiophos	1.00	269	1545	1.440
221	Etaconazole á	8.10	245	1550	1.425
222	Endosulfan II	1.65	195	1550	1.510
223	Sulprofos	1.32	322	1555	1.490
224	Carbofenotion	0.91	157	1570	1.505
225	p,p'-DDT	0.44	235	1575	1.510
226	Piperonyl butoxide	0.14	176	1580	1.415
227	Resmethrin	0.81	171	1590	1.455
228	Propiconazole	4.49	259	1595	1.445
229	Fensulfothion	1.21	293	1595	1.480
230	Benalaxyl	0.13	148	1595	1.545
231	Cyprofuram	0.65	211	1595	1.545
232	Propargite	99.22	350	1600	1.440
233	Propiconazole	1.71	259	1600	1.455
234	Benodanil	1.32	231	1600	1.710
235	Fenthion sulfoxide	1.16	279	1605	1.560
236	Triazophos	1.37	161	1605	1.610
237	Diflufencian	0.93	266	1610	1.370
238	o,p'-Methoxychlor	2.49	227	1610	1.615
239	Cyanophenphos	2.78	303	1615	1.533
240	Edifenphos	0.45	109	1615	1.690
241	Tebuconazole	1.51	250	1625	1.460
242	Oxadixyl	0.51	132	1625	1.615
243	Bifenthrin	0.24	181	1630	1.410
244	Endosulfan sulfate	4.04	387	1630	1.545
245	Nuarimol	1.87	314	1630	1.605
246	Norflurazon	2.20	303	1640	1.545
247	Lenacil	0.36	153	1640	1.740
248	p,p'-Methoxychlor	1.30	227	1665	1.760
249	Fenpropathrin	3.10	181	1675	1.515
250	Phenothrin	0.56	183	1675	1.595
251	Tetramethrin	0.33	164	1680	1.590
252	Chloridazone	6.23	221	1685	1.975
253	Hexazinone	0.68	171	1690	1.735
254	Pyridafenthion	2.27	199	1695	1.745
255	Cinerin II	16.42	107	1705	1.505
256	Mirex	0.60	272	1710	1.870
257	Bifenox	28.44	314	1715	1.720
258	Leptophos	2.02	377	1720	1.885
259	Fosmet	1.20	160	1725	1.910
260	Tetradifon	0.65	229	1730	1.775
261	Trifenmorph	4.56	243	1740	2.045
262	Phosalon	4.14	182	1750	1.780
263	Pyrazophos	1.64	221	1770	1.830
264	Fenarimol	2.23	139	1770	2.025
265	Azinophos-methyl	6.24	160	1775	2.175
266	Permethrin	4.71	183	1780	1.970
267	Bitertanol	2.55	170	1800	2.015
268	Pyridaben	1.35	147	1805	2.015
269	Azinphos-ethyl	2.30	132	1805	2.235
270	Cyfluthrin	69.27	163	1835	2.070
271	Prochloraz	10.45	180	1840	2.035
272	Cyfluthrin	15.18	163	1840	2.075
273	Cyfluthrin:2	11.55	163	1845	2.095
274	Cyfluthrin:3	9.89	163	1850	2.120
275	Cyfluthrin:4	12.59	163	1855	2.140

LECO®

Life Science and Chemical Analysis Solutions

Delivering the Right Results

Analyte	Compound Name	LOD* (pg/µl)	Quant Mass	1st Dim. R.T. (s)	2nd Dim. R.T. (s)
276	Cypermethrine	41.32	181	1860	2.300
277	Decachlorobiphenyl	4.26	498	1860	2.420
278	Cypermethrin	22.33	181	1865	2.335
279	Quinofop-ethyl	14.03	372	1865	2.535
280	Cypermethrine:2	18.51	181	1875	2.370
281	Fluvalinate	5.62	250	1935	2.535
282	Fenvalerate	9.95	167	1935	2.890
283	Fluvalinate:2	4.05	250	1940	2.555
284	Fenvalerate à	41.70	167	1940	2.890
285	Fluvalinate:3	6.66	250	1945	2.605
286	Fenvalerate:2	9.77	167	1955	3.060
287	Difenoconazole:2	19.15	265	2005	3.815

**LOD is expressed as three times the noise.*

LECO Corporation • 3000 Lakeview Avenue • St. Joseph, MI 49085 • Phone: 800-292-6141 • Fax: 269-982-8977
info@leco.com • www.leco.com • ISO-9001:2000 • No. FM 24045 • *LECO is a registered trademark of LECO Corporation.*

Form No. 203-821-327 7/07-REV0