Determination of 277 Pesticides at Trace Levels by GC–TOFMS

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

Key Words: 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 GC-TOFMS method for the trace analysis of pesticides in food stuffs.

2. Instruments and Methods

In this study, measurements were made with a LECO Pegasus® GC–TOFMS system. This system consists of an Agilent 6890N gas chromatograph with a LECO Pegasus Time-of-Flight Mass Spectrometer (TOFMS) as a detector. For all analyses in this study, the analytical column was a 30 m x 0.25 mm ID x 0.25 µm df DB-5ms. Helium was used as a carrier gas at a constant flow of 1.4 mL/minute. The transfer line to the TOFMS consisted of the last 20 cm of the analytical column. The detector was optimized to have a signal-to-noise ratio >1000 for a 200 pg/µl injection of hexachlorobenzene. Data are acquired with a mass range of 50 to 550 amu, an acquisition rate of 10 spectra/second at a detector voltage of 1850 V. In this one-dimensional separation, the temperature program of the GC was as follows.

Rate (°C/min)	Target Temp (°C)	Duration (min)
Initial	95	1.50
20	190	0.00
5	230	0.00
25	300	20.00

For all quantitative work, pesticides standards in the range of 2.5 to 1000 pg/µl were prepared in acetonitril. Injections of 2 µl were performed by a CTC CombiPAL with a Gerstel CIS4 PTV injector in splitless mode at a temperature of 40°C. After 0.25 minutes the injector was heated to 280°C (held for 8 minutes) at a rate of 12°C/second.

3. Results

First, after analysis of the analytical standards (n=7), for all pesticides the average retention time was determined for 500 pg/µL (see Figure 1 for TIC chromatogram). This standard was used as a reference standard for further work. For all pesticides the analytical data as determined are shown in Table 1.

As can be expected, many coelutions do occur. Figure 2 shows an example of how the True Signal Deconvolution™ algorithm of the ChromaTOF® software can be used to identify coeluting peaks, delivering true peak spectra.

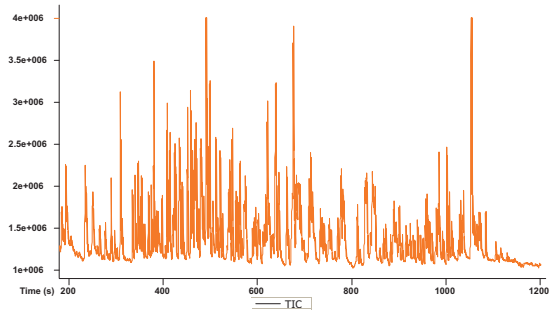

Figure 1. TIC chromatogram showing all pesticides studied.

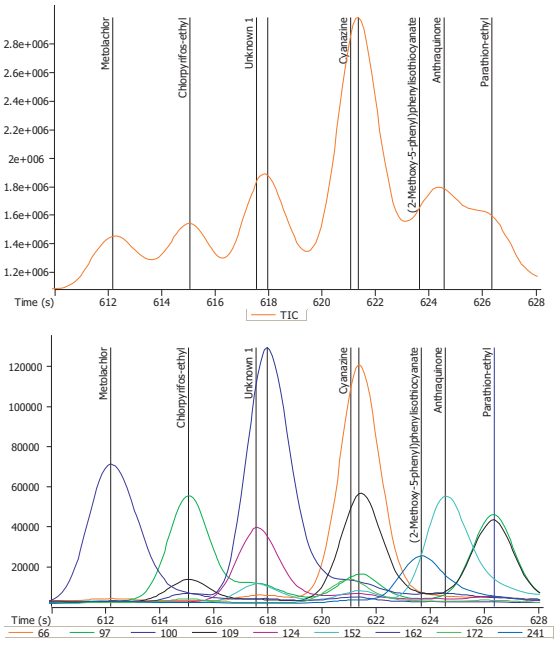

Figure 2. Zoomed TIC and EIC of coeluting compounds. Peak identifications are displayed at the peak markers.

4. Conclusions

It is shown in this work that the LECO Pegasus GC–TOFMS equipped with a Gerstel CIS4 PTV injector is able to analyze hundreds of pesticides at trace levels (down to 10 ppb) in a single run. This work is advantageous to the food and flavor industry where pesticide contamination poses severe health risks. The ability to acquire full mass range spectra allows ChromaTOF software to perform True Signal Deconvolution, enabling peak finding, identification, and quantification of overlapping pesticides.

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.

Life Science and Chemical Analysis Solutions

Delivering the Right Results

Table 1. Pesticides analytical data.

Analyte	Compound Name	LOD* (pg/µl)	Absolute R.T. (s)	Quant Mass
1	o-Cresol	1.07	184.594	108
2	p-Cresol	5.21	192.779	107
3	m-Cresol	2.29	193.294	107
4	Omethoate	21.49	203.979	110
5	Aniline, 2,5-dimethyl-	17.94	233.549	106
6	2,5'-Dimethylaniline	0.71	234.294	121
7	m/p-Chloroaniline	2.10	250.479	127
8	Methamidophos	25.56	258.879	94
9	Dichlorvos	32.72	264.779	109
10	Dichlorfos	16.67	264.894	185
11	Bendiocarb	3.38	276.779	126
12	Dichlobenil	1.70	308.979	171
13	ETPC	1.74	312.994	128
14	3,5-Dichloroaniline	4.64	334.479	161
15	Mevinphos-trans	9.89	339.979	127
16	Ethiofencarb - M	3.44	342.094	168
17	3,4-Dichloraniline	6.68	345.979	161
18	Chlormephos	2.31	346.879	121
19	Vernolate	1.27	349.194	128
20	Etridiazole	1.09	351.694	211
21	Propham	3.11	354.194	179
22	Bromophos-ethyl	35.66	356.394	242
23	Methacrifos	5.77	357.394	180
24	a-HCH	1.50	357.694	181
25	Methacrifos:2	1.53	368.294	180
26	Crimidine	2.34	374.694	171
27	Tebuthiuron	14.19	379.479	156
28	o-Phenylphenol	2.90	379.979	170
29	Benzene, pentachloro-	0.55	380.394	250
30	b-HCH	1.10	385.894	181
31	Methiocarb	1.29	389.594	168
32	TEPP	149.99	391.979	161
33	Phenol, 2,3,4,5-tetrachloro-	25.45	392.594	232
34	ETU	75.27	393.194	102
35	Methomyl	56.87	394.479	105
36	Heptenophos	7.67	397.279	124
37	Chlorfenprop-methyl	4.06	407.779	165
38	Tecnazene	2.70	408.294	261
39	Thionazin	2.07	411.294	143
40	Propoxur	217.64	412.894	110
41	Propachlor	0.99	413.894	120
42	Demeton-O	20.13	413.979	115
43	Demeton-S-methyl	20.19	419.779	109
44	Fluometuron	4.96	420.879	72
45	Diphenylamine	0.84	423.294	169
46	Tributyl phosphate	1.21	425.094	155
47	Ethoprofos	3.41	425.179	158
48	Cycloate	1.62	427.194	154
49	2,4,5-Trimethacarb	72.69	433.179	121
50	Trifluralin	1.38	434.594	264
51	Chlordimeform	6.77	435.579	181
52	Dicrotophos	4.39	436.194	127
53	Dichlofluanid-Metabolitit (DMSA)	25.86	436.379	200
54	Sulfotep	7.30	440.579	322
55	Monocrotophos cis/trans	21.65	443.179	127
56	Diallate cis	2.97	451.794	234
57	Phorate	2.69	452.494	121
58	Diallate trans	4.38	460.594	234
59	Hexachlorobenzene (HCB)	0.87	461.994	284
60	Thiometon	4.54	464.179	125
61	Anisole, 2,3,4,5,6-pentachloro-	5.67	466.779	237
62	Demeton-S	2.64	467.794	88
63	Dimethoate	8.26	469.094	125
64	Dichloran	4.23	469.794	206
65	2,3,5-Trimethacarb	58.46	469.879	121
66	Ethoxyquin	10.86	471.694	202
67	Carbofuran	340.51	473.079	164
68	Simazine	18.86	474.979	201
69	Atrazine	7.30	479.179	200
70	Chlorbufam	31.05	479.594	127
71	Monolinuron	7.40	480.594	126
72	Dimethipin	78.15	481.179	118
73	Propazine	3.27	482.694	172
74	Cyromazine	42.38	483.494	151
75	Quintozen	14.51	485.479	142
76	Benazolin	31.05	487.594	170
77	Tolylfluanid-Metabolit (DMST)	37.88	488.494	214
78	Dioxathion	85.19	488.894	270
79	Propetamphos	2.03	490.894	194
80	g-HCH	0.81	491.194	181
81	Triethazine	5.02	491.479	200
82	Terbutylazine	1.79	493.394	214
83	Cyanophos	3.84	493.979	109
84	Propyzamide	5.88	496.879	173
85	Diazinon	1.69	498.479	137
86	Fonofos	1.05	498.879	109
87	Pyrimethanil	1.01	505.394	198
88	Dimethirimol	13.58	505.858	166
89	Disulfoton	14.40	512.294	153
90	Terbacil	3.37	513.694	161
91	Fenfuram	5.68	515.994	201
92	Triallate	19.36	520.379	268
93	d-HCH	14.92	521.394	181
94	Pirimicarb	1.86	526.094	166
95	Tridemorph	43.30	532.079	128
96	Formothion	106.89	535.479	125
97	Metobromuron	23.54	538.079	170
98	Pentachloroaniline	9.41	539.479	265
99	Endosulfan ether	1.24	541.879	69
100	Phosphamidon (Z)	2.45	542.694	127
101	Dichlofenthion	9.50	546.279	223
102	Dimethachlor	2.25	546.994	197
103	Chlorpyrifos-methyl	3.60	553.994	286
104	Metribuzin	6.36	554.179	198
105	Vinclozoline	9.65	558.179	124
106	Methyl parathion	22.01	562.094	263
107	Alachlor	12.84	562.794	188
108	Tolclofos-methyl	4.05	563.379	265
109	Fuberidazole	22.74	567.494	184
110	Carbaryl	48.06	570.079	144
111	Metalaxyl	8.65	571.479	132
112	Ametryn	16.48	572.394	227
113	Heptachlor	9.20	574.094	272
114	Fenchlorphos	4.18	575.394	285
115	Paraoxon	17.96	577.179	109
116	Demeton-S-methylsulfone	466.25	584.179	169
117	Propargit-Metabolit	5.03	585.579	135
118	Pirimiphos methyl	15.26	589.479	180
119	Terbutryn	5.41	592.579	170
120	Fenitrothion	18.13	593.794	277
121	Ethofumesate	6.61	596.279	161
122	Bromacil	0.62	598.179	205
123	Linuron	8.80	601.679	61
124	Malathion	29.16	605.494	173
125	Metolachlor	9.90	611.979	238
126	Chlorpyrifos-ethyl	12.07	614.894	199
127	Diethofencarb	12.26	617.379	168
128	Benthiocarb	1.69	617.894	100
129	Cyanazine	37.01	620.794	225
130	Fenthion	3.67	621.394	278
131	Anthraquinone	7.99	624.394	180
132	Parathion-ethyl	23.42	626.294	291
133	Triadimefon	15.81	630.279	208
134	Carbetamide	138.82	632.979	119
135	Chlorthion	15.50	636.679	109
136	Nitrothal-isopropyl	7.95	636.794	212
137	Telodrin	1.88	638.894	103
138	Trichloronat	5.03	639.294	269
139	Crufomate	28.43	639.679	182
140	Butralin	9.31	639.994	266
141	Fenson	3.94	645.279	141
142	Pirimiphos ethyl	12.63	645.794	168
143	Dodemorph-cis	7.70	649.294	154
144	Isodrin	4.19	662.479	195
145	Metazachlor	2.44	665.694	132
146	Penconazole	7.60	671.879	159
147	Endosulfan sulfate	13.92	673.779	239
148	Chlozolinate	32.10	674.394	188
149	Isofenphos	7.99	676.279	213
150	Oxychlordane	7.12	676.694	154
151	Heptachlor epoxide	22.37	677.094	353
152	trans-Chlorfenvinphos	17.07	678.594	267
153	Mecarbam	29.30	682.194	131
154	Bioallethrin	16.58	684.794	123
155	Phenthoate	8.59	686.779	125
156	Pyrethrin	15.35	687.079	123
157	Quinalphos	5.49	688.279	146
158	Tiabendazole	42.16	689.394	174
159	Procymidone	14.09	692.479	283
160	Triflumizole	6.84	696.179	73
161	Crotoxyphos	76.27	698.779	166
162	Triadimenol	11.68	705.679	112

Analyte	Compound Name	LOD* (pg/µl)	Absolute R.T. (s)	Quant Mass
163	Bromophos-ethyl	7.00	709.794	145
164	Chlordane , trans	3.96	713.394	125
165	Chinomethionat	40.97	715.379	206
166	o,p'-DDE	7.19	717.179	246
167	Tetrachlorvinphos	30.55	719.679	329
168	Vamidothion	60.67	721.094	145
169	Paclobutrazide	16.68	722.579	236
170	Endosulfan I	14.02	733.579	195
171	Ditalimfos	6.12	736.779	130
172	Diethatyl ethyl	10.62	737.479	188
173	Flutriafol	3.24	741.179	123
174	Bromfenvinphos	16.83	741.879	267
175	Fenamiphos	13.61	744.779	154
176	Jodfenphos	10.68	750.594	377
177	Chlorfenson	12.91	752.894	175
178	Imazalil	14.26	753.479	215
179	Prothiofos	26.34	756.894	309
180	Profenofos	92.36	764.594	208
181	DDE p,p'-	9.10	770.894	246
182	Flamprop-methyl	1.55	775.579	105
183	Myclobutanil	5.82	777.879	179
184	Dieldrin	11.65	777.894	263
185	o,p'-DDD	7.02	781.279	235
186	Bupirimate	19.48	783.579	273
187	Buprofezin	9.97	784.094	172
188	Diclobutrazol	6.74	787.079	147
189	Cinerin	40.88	790.779	123
190	Binapacryl	366.26	798.379	83
191	Nitrofen	28.46	812.294	283
192	Endrin	40.76	812.794	263
193	Fluazifop-butyl	10.97	818.194	282
194	Chlorobenzilate	2.38	828.794	139
195	Fenthion sulfoxide	40.22	830.994	279
196	Flamprop-methyl:2	1.40	831.279	105
197	Fensulfothion	18.58	831.994	293
198	Endosulfan II	22.39	832.594	195
199	Etaconazole cis	16.93	833.779	173
200	Oxadixyl	5.57	839.979	132
201	Etaconazole trans	11.95	840.379	173
202	DDD p,p'-	3.83	843.894	235
203	Ethion	7.12	845.579	231
204	DDT p,p'-	1.23	846.994	235
205	Chlorthiophos iii	11.57	849.479	269
206	Chlorthiophos	9.04	849.594	269
207	Benodanil	10.92	859.894	231
208	Tetrasul	14.03	867.579	252
209	Triazophos	12.50	872.094	161
210	Sulprofos	5.16	872.679	156
211	Pyrethrin	55.01	878.779	123
212	Benalaxyl	2.26	882.894	148
213	Carbophenothion	4.10	887.379	157
214	Norflurazon	12.97	889.079	145
215	Cyanophenphos	5.32	889.879	157
216	Edifenphos	19.54	890.379	109
217	Propiconazole cis	15.78	892.479	173
218	Propiconazole cis	50.68	892.694	259
219	Lenacil	13.62	896.794	153
220	Chloridazon	45.17	899.394	221
221	Propiconazole trans	5.48	900.379	173
222	Propiconazole trans	42.06	900.594	259
223	o,p'-DDT	2.71	901.694	235
224	Hexazinone	2.69	907.594	171
225	Nuarimol	4.39	915.079	139
226	Tebuconazole	16.70	918.179	250
227	Propargite I	34.49	922.073	201
228	Propargite II	56.37	923.979	201
229	Diflufenicam	2.45	924.294	266
230	Piperonyl butoxide	4.38	930.379	176
231	Benzoylprop ethyl	1.16	939.594	105
232	Pyridafenthion	47.79	945.879	340
233	Tetramethrin	21.15	951.194	164
234	Phosmet	1.83	951.994	160
235	Bifenthrin	1.03	956.794	181
236	Bromopropylate	10.35	956.994	341
237	Tetramethrin:2	2.64	959.494	164
238	Methoxychlor	3.26	961.979	227
239	Fenpropathrin	33.43	965.279	181
240	Bifenox	132.70	970.879	314
241	Furathiocarb	353.79	977.379	194
242	Phenothrin	2.85	977.794	183
243	Tetradifon	10.23	979.279	159
244	Phenothrin:2	1.69	982.994	183
245	Phosalone	2.23	984.694	182
246	Leptophos	1.61	985.294	171
247	Azinphos-Methyl	14.15	987.694	160
248	Mirex	1.38	1001.89	272
249	Fenarimol	11.85	1006.98	221
250	Azinphos-ethyl	5.52	1012.48	160
251	Dialifos	17.69	1014.98	208
252	Bitertanol B	1.02	1028.39	170
253	Permethrin	1.09	1031.19	183
254	Bitertanol B:2	24.32	1032.59	248
255	Coumaphos	13.12	1035.29	226
256	Permethrin:2	3.66	1035.99	183
257	Pyridaben	2.62	1037.18	147
258	Prochloraz	11.09	1037.69	180
259	Cyfluthrin	32.50	1051.68	163
260	Cyfluthrin:2	33.05	1056.18	163
261	Cyfluthrin:3	164.10	1058.38	163
262	Cyfluthrin:4	126.99	1059.98	163
263	Cypermethrin	95.83	1065.28	181
264	Cypermethrin:2	123.77	1069.78	181
265	Cypermethrin:3	106.83	1071.98	181
266	Quinofop-ethyl	13.51	1073.08	299
267	Fluvalinate	249.14	1076.68	250
268	Decachlorobiphenyl (PCB 209)	17.30	1084.28	498
269	Fenvalerate à	147.63	1106.08	167
270	Fenvalerate à	463.74	1106.39	225
271	Fluvalinate:2	209.51	1114.38	250
272	Esfenvalerate	207.61	1116.38	167
273	Fenvalerate à:2	448.34	1116.64	225
274	Difenoconazole cis	14.59	1129.89	323
275	Difenoconazole trans	18.47	1133.19	323
276	Deltamethrin	74.69	1135.23	181
277	Deltamethrin:2	260.29	1146.22	181

*LOD is expressed as three times the noise.

Life Science and Chemical Analysis Solutions

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. 203-821-326 7/07-REV0