Evaluation of benefits and drawbacks of reducing injection volume in LC-MS/MS

Table of Contents

1. Aim and scope

This document evaluates the impact that the reduction of volumes of injection in LC-MS/MS has on performance, maintenance of the equipment.

2. Short description

The evaluation is performed by study of the response of 276 pesticides, most of them included in the European Union Multi Annual Control Program and the Working Document SANCO/12745/2013, injecting analytical standards at 0.01 mg/L in three different matrices (tomato, onion and raisins) and with three volumes of injection: 1.5 µL, 2.5 µL and 5 µL.

3. Apparatus and consumables

- Automatic pipettes, suitable for handling volumes of 10 µL to 5000 µL and 1 mL to 5 mL
- 50 ml and 15 ml PTFE centrifuge tubes
- Vortex
- Shaker
- Evaporation device coupled to a flow of nitrogen
- Centrifuge, suitable for the centrifuge tubes employed in the procedure and capable of achieving at least 3300 rpm
- Injection vials, 2 ml, suitable for LC auto-sampler

4. Chemicals

- Acetonitrile ultra-gradient.
- Trisodium citrate dihydrate
- Disodium hydrogenocitratesesquihydrate
- Sodium chloride
- Anhydrous magnesium sulphate
- Primary secondary amine (PSA)
- Ammonium formate
- Ultra-pure water
- Acetonitrile LC-MS grade
- Formic acid
- Pesticide analytical standards

5. Procedure

5.1. Extraction procedure

Following Document No. SANTE/2019/12682, the samples were homogenised by cryogenic milling.

QuEChERS

1. Weigh 10 g in 50 mL PTFE centrifuge tube.

   a. 10 ± 0.1 g of sample for matrices with high water content (tomato and onion).

   b. 5 ± 0.1 g of sample + 7.5 mL of water, for matrix with high sugar and low water content (raisin).

2. Add 10 mL of acetonitrile and 10 µL of 10 mg/L carbendazim-d3, malathion-d10 and TPP (procedure internal standards).
3. Shake the sample using an automatic axial shaker for 4 min.
4. Add 4 g of magnesium sulphate, 1 g of sodium chloride, 1 g of trisodium citrate dihydrate and 0.5 g of disodium hydrogenocitrate sesquihydrate.
5. Shake the samples again in the automatic shaker for 4 min.
6. Centrifuge the tubes at 3700 rpm for 5 min.
7. Transfer 5 mL of the supernatant to a 15 mL PTFE tube containing 750 mg magnesium sulphate and 125 mg PSA.
8. Vortex the tube for 30 sec.
9. Centrifuge the tubes at 3700 rpm for 5 min.
10. Add 40 µL of formic acid 5% in acetonitrile to option a in step 7.
11. Preparation of vials: dilute 100 µL black extract (spiked with 0.01 mg/L analytical standards) with 400 µL of water containing dimethoate-d6 at 0.050 mg/L (Injection Internal Standard). This way, 1 mL of extract contains 0.2 g of sample for high water content matrices, and 0.1 g of sample for low water and high sugar content matrices.

5.2. Sequence of analysis

In order to evaluate the impact of reducing the volume of injection, a sequence of 50 samples was analysed for each matrix at the three studied volumes of injection. Therefore, the following sequences were analysed:

- 50 x 0.01 mg/L mix pesticides in **tomato** extract. Volume of injection: **1.5 µL**.

- 50 x 0.01 mg/L mix pesticides in **tomato** extract. Volume of injection: **2.5 µL**.
- 50 x 0.01 mg/L mix pesticides in **tomato** extract. Volume of injection: **5 µL**.
- 50 x 0.01 mg/L mix pesticides in **onion** extract. Volume of injection: **1.5 µL**.
- 50 x 0.01 mg/L mix pesticides in **onion** extract. Volume of injection: **2.5 µL**.
- 50 x 0.01 mg/L mix pesticides in **onion** extract. Volume of injection: **5 µL**.
- 50 x 0.01 mg/L mix pesticides in **raisins** extract. Volume of injection: **1.5 µL**.
- 50 x 0.01 mg/L mix pesticides in **raisins** extract. Volume of injection: **2.5 µL**.
- 50 x 0.01 mg/L mix pesticides in **raisins** extract. Volume of injection: **5 µL**.

After each sequence, the source was checked and cleaned. The list of studied pesticides is shown in **Appendix I**.

5.3. Instrumentation and analytical conditions for the LC- MS/MS system

The LC system was operated in multiple reaction monitoring mode (MRM). Selected reaction monitoring (SRM) experiments were carried out to obtain the maximum sensitivity for the detection of the target molecules. For confirmation of the studied compounds, two SRM transitions and a correct ratio between the abundances of the two optimized SRM transitions (SRM2/SRM1) were used, along with retention time matching. The mass transitions used are presented in **Appendix I.**

5.3.1. UHPLC (SCIEX Exion LC)

- Column: Zorbax Eclipse Plus C8 2.1x100 mm and 1.8 µm particle size (Agilent)
- Mobile phase A: Water (0.1 % formic acid, 5 mM ammonium formate, 2 % MeOH)
- Mobile phase B: Methanol (0.1 % formic acid, 5 mM ammonium formate, 2 % water)
- Column temperature: 35 °C
- Flow rate: 0.3 mL/min
- Injection volume: 1.5, 2.5 and 5 µL

Mobile phase gradient for pesticides analysis:

Time [min]	Mobile phase A	Mobile phase B
0	100 %	0 %
1	90 %	10 %
2	70 %	30 %
3	50 %	50 %
11	0 %	100 %
14	0 %	100 %
14.1	100 %	0 %
17	100 %	0 %

5.3.2. Triple quadrupole system (SCIEX 6500+)

Ionisation mode: polarity switching

- Positive polarity:
  - Curtin gas: 25
  - Collision gas: 7
  - IonSpray Voltage: 5500
  - Temperature: 300
  - Ion source gas 1: 40
  - Ion source gas 2: 50
- Negative polarity:
  - Curtin gas: 25
  - Collision gas: 7
  - IonSpray Voltage -4500
  - Temperature: 300
  - Ion source gas 1: 40
  - Ion source gas 2: 50

6. Results

The evaluation of the reduction of the amount of matrix introduced into the instrument was studied in terms of identification and sensitivity.

As regards identification, all the compounds were identified in the three studied matrices at a volume of injection of 5 µL. When the volume was reduced to a half, 2.5 µL, the identification capabilities slightly decreased, as can be observed in **Table 1.** When injecting 1.5 µL, raisins was the matrix more affected, with a loss of 9 % of the identified compounds.

Table 1. Percentage of identified compounds (Total number of compounds: 276)

Matrix	1.5 µL	2.5 µL	5 µL
Tomato	97 %	99 %	100 %
Onion	97 %	99 %	100 %
Raisins	91 %	98 %	100 %

The impact that introducing less amount of matrix has on the instrumental response was studied by comparison of the chromatographic areas. **Figure 1** shows the average instrumental response of the 276 studied compounds for each volume of injection. The reduction of the response could be expected to be 50 % when comparing 5 µL vs 2.5 µL, and 33 % when comparing 5 µL vs 1.5 µL. However, the reduction of the amount of matrix has a positive impact on the relative response, which is higher than 50 % or 33 % (when comparing 5 µL vs 2.5 µL or 1.5 µL, respectively), and proving the effectiveness of this approach. The individual relative responses in relation to the 5 µL response are shown in **Tables 1**, **2** and **3** of **Appendix II.** Ion source cleaning after was necessary after the injection series of 5 uL of raisins extracts. The injection of 2.5 ul can avoid the use of clean up step as the same results were obtained except in the case of raisins

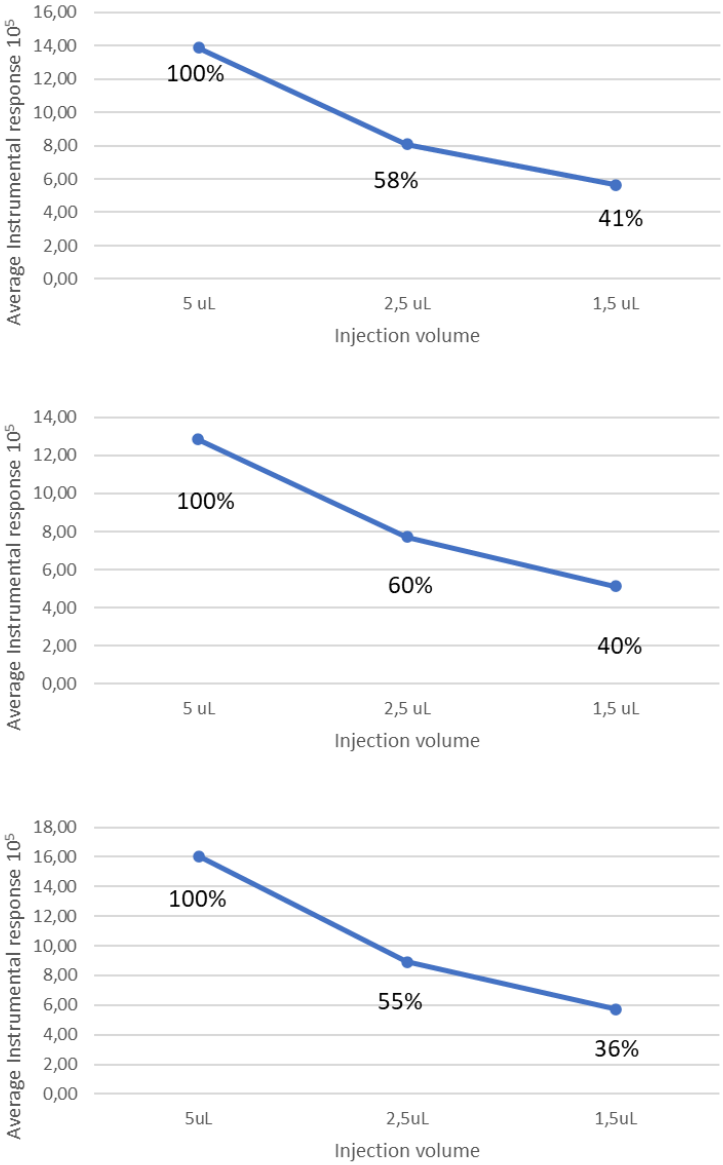

Figure 1. Average instrumental response of the 276 studied compounds vs injection volume of 0.01 mg/L standard mixes in **a)** tomato, **b)** onion **c)** raisin.

Another way of showing this positive effect in the sensitivity is by normalising the areas with the one at 5 µL. **Figure 2** shows the normalised chromatographic responses in the three matrices and for the three injection volumes evaluated. This graph shows an increase of relative responses around 15 % by decreasing the volume from 5 to 2.5 µL, and around 25 % in case of 1.5 µL. It´s important to note that the majority of the new instruments acquired by the OfLs nowadays can achieve such performance.

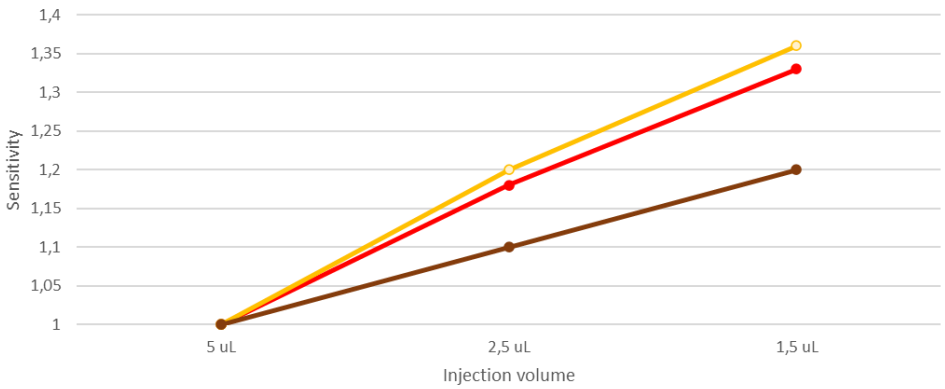

Figure 2. Normalised average chromatographic responses (red-tomato, yellow-onion, brown-raisins) for the three injection volumes evaluated.

7. Conclusions

Injection of volumes lower than 5 µL are recommendable as the LOQs are not negatively impacted and the maintenance of the instrument is much lower. Furthermore, clean up steps could be avoided except in case of very complex matrices such as raisins, reducing the cost and time per analysis.

8. References

- Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Document Nº SANTE/2019/12682.
- http://www.eurl-pesticides.eu

APPENDIX I: MASS TRANSITIONS

Detection and chromatographic parameters for the selected compounds analysed by LC-MS/MS.

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
1	2.4-D	6.56	219	161	163	-15	-15	Negative
2	8-Quinolinol	6.22	146	128	118	33	31	Positive
3	Acephate	3.44	184	143	95	13	33	Positive
4	Acetamiprid	4.63	223	126	90	27	49	Positive
5	Acrinathrin	11.24	559	208	181	21	51	Positive
6	Alachlor	8.42	270	238	162	17	29	Positive
7	Albendazole	7.16	266	234	191	27	49	Positive
8	Aldicarb	5.45	116	89	70	13	13	Positive
9	Aldicarb sulfoxide	3.63	207	132	89	9	23	Positive
10	Ametoctradin	9.56	276	176	149	51	49	Positive
11	Anilofos	9.1	368	199	125	19	45	Positive
12	Atrazine	6.81	216	174	104	25	39	Positive
13	Avermectin b1a	11.02	890	305	307	35	29	Positive
14	Avermectin b1b	10.84	876	553	291	21	33	Positive
15	Azinphos methyl	7.15	318	132	77	23	51	Positive
16	Azinphos ethyl	8.25	345	132	160	25	13	Positive
17	Azoxystrobin	7.40	404	372	344	21	35	Positive
18	BAC10	8.10	276	91	184	53	27	Positive
19	BAC8	6.67	248	91	156	43	27	Positive
20	Benalaxyl	9.13	326	148	294	29	15	Positive
21	Bendiocarb	6.02	224	167	109	13	23	Positive
22	Benzivindiflupyr	9.03	398	342	322	25	33	Positive
23	Bifenazate	8.18	301	198	170	15	39	Positive
24	Bifenthrin	11.66	440	181	165	17	103	Positive
25	Bitertanol	9.25	338	269	99	15	21	Positive
26	Bixafen	8.73	414	394	266	21	33	Positive
27	Boscalid	7.73	343	271	140	35	35	Positive
28	Bromacil	6.04	261	205	188	19	41	Positive
29	Bromuconazole I	8.10	378	161	159	37	37	Positive
30	Bromuconazole II	8.83	378	159	161	37	37	Positive
31	Bupirimate	8.50	317	166	210	33	33	Positive
32	Buprofezin	10.22	306	201	116	17	23	Positive

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
33	Butoxycarboxim	3.72	223	106	65	13	23	Positive
34	Carbaryl	6.22	202	145	127	17	41	Positive
35	Carbendazim	4.18	192	160	132	25	41	Positive
36	Carbendazim d3	4.15	195	160	132	23	43	Positive
37	Carbofuran	5.97	222	165	123	19	31	Positive
38	Chlorantraniliprole	7.15	482	451	284	29	19	Positive
39	Chlorbromuron	7.76	295	206	182	27	25	Positive
40	Chlorfenvinphos	9.22	359	155	170	17	59	Positive
41	Chlorfluazuron	10.81	542	385	158	31	27	Positive
42	Chloridazon	4.77	222	104	92	31	33	Positive
43	Chlorotoluron	6.62	213	72	140	23	35	Positive
44	Chloroxuron	8.81	291	72	164	47	23	Positive
45	Chlorpyrifos methyl	9.39	322	125	290	29	21	Positive
46	Chlorpyriphos	10.27	352	200	97	29	47	Positive
47	Chromafenozide	8.45	395	175	91	19	87	Positive
48	Clofentezine	9.02	303	138	102	21	51	Positive
49	Clomazone	7.36	240	125	89	27	65	Positive
50	Clopyralid	3.59	192	146	110	27	45	Positive
51	Coumaphos	8.90	363	227	307	35	25	Positive
52	Cyazofamid	8.54	325	108	217	19	33	Positive
53	Cyflufenamid	9.45	414	296	241	21	31	Positive
54	Cyhalofop butyl	9.66	375	256	358	25	11	Positive
55	Cymoxanil	4.96	199	128	111	13	25	Positive
56	Cyproconazole I	8.10	292	70	125	45	43	Positive
57	Cyproconazole II	8.35	292	70	125	45	43	Positive
58	Cyprodinil	8.49	226	93	108	53	35	Positive
59	Cyromazine I	2.63	167	125	83	25	29	Positive
60	Cyromazine II	3.08	167	125	83	25	29	Positive
61	Dazomet	4.00	163	90	120	10	10	Positive
62	DEET	6.98	192	119	91	25	39	Positive
63	Deltamethrin	10.98	522	506	281	15	23	Positive
64	Demeton-S-methyl	4.03	263	169	109	21	37	Positive
65	Demeton-S-methylsulfoxide	3.93	247	169	109	19	37	Positive
66	Desethylterbuthylazine	6.29	202	146	104	23	37	Positive
67	Diazinon	9.16	305	169	153	29	29	Positive
68	Dichlorvos	6.00	221	19	79	25	37	Positive
68	Dichlorvos-d6	5.98	227	115	151	25	19	Positive
69	Dicrotophos	4.28	238	112	193	17	15	Positive

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
70	Diethofencarb	7.32	268	226	124	15	43	Positive
71	Difenoconazole	9.41	406	251	188	35	61	Positive
72	Difenoxuron	6.77	287	123	72	27	49	Positive
73	Diflubenzuron	8.54	309	156	289	-16	-14	Negative
74	Dimethoate	4.82	230	199	125	13	29	Positive
75	Dimethoate-d6	4.80	236	205	131	10	10	Positive
76	Dimethomorph I	7.56	388	301	165	29	43	Positive
77	Dimethomorph II	7.83	388	301	165	29	43	Positive
78	Dimethylvinphos-Z	8.22	331	127	170	17	57	Positive
79	Diniconazole	9.60	326	70	159	67	43	Positive
80	Dinotefuran	3.65	203	129	113	17	15	Positive
81	Dithianon	7.48	296	264	251	-32	-50	Negative
82	Diuron	7.02	233	72	160	21	37	Positive
83	Dodine	9.20	228	186	71	27	27	Positive
84	Edifenphos	8.96	311	283	109	19	45	Positive
85	Emamectin b1a	9.95	886	158	82	41	117	Positive
86	Emamectin b1b	9.69	872	158	82	41	111	Positive
87	EPN	9.48	324	296	157	19	31	Positive
88	Epoxiconazole	8.41	330	121	101	27	67	Positive
89	Ethiofencarb	6.49	226	107	164	25	11	Positive
90	Ethion	10.21	385	199	143	13	37	Positive
91	Ethiprole	7.77	397	351	255	29	49	Positive
92	Ethirimol	5.61	210	140	98	29	37	Positive
93	Ethoprophos	8.55	243	173	131	21	29	Positive
94	Etofenprox	11.39	394	177	359	19	15	Positive
95	Etoxazole	10.60	360	141	304	37	25	Positive
96	Famoxadone	8.92	375	255	319	23	23	Positive
97	Fenamidone	7.74	313	236	92	21	39	Positive
98	Fenamiphos sulfone	6.07	336	266	308	29	21	Positive
99	Fenamiphos sulfoxide	5.92	320	233	292	31	23	Positive
100	Fenamiphos	8.71	304	217	234	31	23	Positive
101	Fenarimol	8.41	331	268	189	33	65	Positive
102	Fenazaquin	10.81	307	161	131	23	63	Positive
103	Fenbendazole	7.94	300	268	159	33	45	Positive
104	Fenbuconazole	8.55	337	125	70	37	47	Positive
105	Fenhexamid	8.34	302	97	143	31	45	Positive
106	Fenobucarb	7.66	208	95	152	21	13	Positive
107	Fenoxycarb	8.66	302	116	88	15	31	Positive

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
108	Fenpicoxamid	9.76	615	239	515	37	23	Positive
109	Fenpropathrin	10.27	350	97	125	47	17	Positive
110	Fenpropidin	7.18	274	147	117	39	71	Positive
111	Fenpropimorph	7.48	304	147	117	39	77	Positive
112	Fenpyrazamine	8.19	332	230	231	25	17	Positive
113	Fenpyroximate-E	10.71	422	366	138	25	41	Positive
114	Fensulfothion	6.82	309	281	157	21	21	Positive
115	Fenthion	8.88	279	247	169	19	23	Positive
116	Fenthion sulfone	6.28	311	125	279	29	25	Positive
117	Fenthion sulfoxide	6.10	295	280	109	25	39	Positive
118	Fenuron	4.65	165	72	120	19	23	Positive
119	Fipronil	8.85	454	437	368	17	31	Positive
120	Fipronil-sulfoxide	9.16	451	415	282	-24	-38	Negative
121	Flazasulfuron	7.17	408	182	139	29	61	Positive
122	Flonicamid	4.19	230	203	174	25	25	Positive
123	Fluacrypyrim	9.65	427	205	145	15	41	Positive
124	Fluazifop-P	7.60	328	282	254	15	41	Positive
125	Flubendamine	9.02	681	254	274	-34	-24	Positive
126	Flucythrinate	10.56	469	412	199	17	27	Positive
127	Fludioxonil	7.83	266	229	158	19	47	Positive
128	Fluensulfone	6.81	292	166	89	25	35	Positive
129	Flufenacet	8.53	364	153	195	33	33	Positive
130	Flufenacet	8.53	365	153	195	33	33	Positive
131	FLufenoxuron	10.56	489	158	141	25	71	Positive
132	Fluometuron	6.62	233	72	160	23	37	Positive
133	Fluopicolide	8.00	382	173	145	31	75	Positive
134	Fluopyram	8.39	397	208	173	31	41	Positive
135	Fluquinconazole	8.18	376	307	349	35	27	Positive
136	Flusilazole	8.75	316	247	165	25	37	Positive
137	Flutriafol	6.79	302	70	123	45	39	Positive
138	Fluxypyraxad	7.97	382	362	234	23	33	Positive
139	Formetanate hydrochloride	3.46	222	165	120	21	37	Positive
140	Fosthiazate	6.54	289	228	104	15	27	Positive
141	Haloxyfop	8.72	3.62	316	288	25	37	Positive
142	Hexaconazole	9.36	3.14	70	159	49	43	Positive
143	Hexaflumuron	9.65	461	158	141	25	71	Positive
144	Hexythiazox	10.48	353	228	168	21	25	Positive
145	Imazalil	6.54	297	159	201	31	25	Positive

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
146	Imidacloprid	4.43	256	209	175	23	27	Positive
147	Indoxacarb	9.66	528	249	203	23	55	Positive
148	Ioxynil	6.97	370	127	215	-40	-44	Negative
149	Iprodione	8.58	330	245	288	23	21	Positive
150	Iprovalicarb	8.48	321	119	203	33	13	Positive
151	Isocarbophos	6.98	307	321	273	21	11	Positive
152	Isofenfos methyl	8.96	332	231	273	21	9	Positive
153	Isoprocarb	6.86	211	194	95	11	25	Positive
154	Isoprothiolane	7.91	291	231	189	15	27	Positive
155	Isoproturon	6.93	207	72	165	23	21	Positive
156	Kresoxim methyl	8.82	314	267	222	11	23	Positive
157	Lenacil	6.90	235	153	136	23	41	Positive
158	Linuron	7.59	249	160	182	33	33	Positive
159	Lufenuron	10.27	509	339	326	-20	-26	Negative
160	Malathion	8.01	331	137	285	17	11	Positive
161	Malathion-d10	7.96	341	132	100	19	35	Positive
162	Mandipropamid	7.77	412	356	328	15	35	Positive
163	Mebendazole	6.30	296	264	105	31	45	Positive
164	Mepanipyrim	8.03	224	106	77	33	55	Positive
165	Meptyldinocap	10.9	295	134	193	-72	-42	Negative
166	Metaflumizone-E	9.73	507	287	178	35	33	Positive
167	Metaflumizone-Z	10.16	507	287	178	35	33	Positive
168	Metalaxyl	6.96	280	91	77	55	147	Positive
169	Metamitron	4.71	203	175	174	23	23	Positive
170	Metconazole	9.29	320	70	125	53	53	Positive
171	Methamidophos	3.10	142	94	125	19	19	Positive
172	Methidathion	7.13	303	145	85	11	33	Positive
173	Methiocarb	7.71	226	169	121	15	27	Positive
174	Methiocarb sulfone	4.76	275	258	122	13	31	Positive
175	Methiocarb sulfoxide	4.54	242	185	170	21	31	Positive
176	Methomyl	4.01	163	88	106	13	15	Positive
177	Methoxyfenozide	8.19	369	149	313	23	11	Positive
178	Metobromuron	6.66	259	170	148	27	21	Positive
179	Metolachlor	8.62	284	252	176	23	37	Positive
180	Metolcarb	5.66	166	109	94	19	43	Positive
181	Metrafenone	9.36	409	209	227	21	29	Positive
182	Monocrotophos	4.22	224	193	127	11	21	Positive
183	Monolinuron	6.39	215	126	99	27	65	Positive

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
184	Monuron	5.81	199	72	126	21	35	Positive
185	Myclobutanil	8.18	289	70	125	21	49	Positive
186	Neburon	8.88	275	88	114	21	21	Positive
187	Nitenpyram	3.90	271	237	126	27	37	Positive
188	Novaluron	9.83	493	158	141	27	27	Positive
189	Omethoate	3.61	214	183	125	17	27	Positive
190	Orthosulfamuron	6.79	423	268	242	-18	-22	Negative
191	Oxadiargyl	9.31	341	223	230	25	33	Positive
192	Oxadixyl	5.36	279	219	132	17	43	Positive
193	Oxamyl	3.82	237	72	220	37	7	Positive
194	Oxasulfamuron	5.49	407	150	107	15	27	Positive
195	Oxathiapipronil	7.84	540	500	522	35	37	Positive
196	Oxyfendazole	5.43	316	159	191	43	29	Positive
197	Oxyfluorfen	10.04	362	316	237	21	37	Positive
198	Paclobutrazol	7.99	294	70	125	47	51	Positive
199	Penconazole	9.02	284	159	70	41	21	Positive
200	Pencycuron	9.51	329	125	89	31	91	Positive
201	Pendimethalin	10.37	282	212	194	17	25	Positive
202	Penflufen	8.95	318	234	141	23	21	Positive
203	Penthiopyrad	9.12	360	276	177	29	63	Positive
204	Phenthoate	8.85	321	247	135	21	37	Positive
205	Phosalone	9.28	368	182	111	19	57	Positive
206	Phosmet	7.23	318	160	133	25	49	Positive
207	Phoxim	9.21	299	129	77	17	47	Positive
208	Pirimicarb	5.84	239	182	72	23	37	Positive
209	Pirimicarb-desmethyl	4.61	225	168	72	21	35	Positive
210	Pirimiphos-methyl	9.25	306	164	108	31	39	Positive
211	Prochloraz	9.01	376	308	266	17	23	Positive
212	Procymidone	8.27	284	256	145	25	55	Positive
213	Profenofos	9.94	373	303	345	25	19	Positive
214	Promecarb	7.95	208	151	109	13	23	Positive
215	Prometryn	7.97	242	158	200	33	27	Positive
216	Propamocarb	3.68	189	102	144	23	19	Positive
217	Propaquizafop	9.93	444	100	371	23	23	Positive
218	Propargite	10.63	368	231	175	15	23	Positive
219	Popazine	7.66	230	146	188	33	25	Positive
220	Propiconazole I	9.08	342	159	123	41	77	Positive
221	Prociconazole II	9.18	342	159	123	41	77	Positive

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
222	Propoxur	5.96	210	111	168	21	13	Positive
223	Propyzamide	8.04	257	191	190	21	21	Positive
224	Proquinazid	10.59	373	331	289	23	33	Positive
225	Prosulfocarb	9.80	252	91	128	39	17	Positive
226	Prothioconazole	9.16	315	306	125	-24	-32	Negative
227	Prothiofos	11.05	345	241	269	25	17	Positive
228	Pymetrozine	3.47	218	105	78	27	57	Positive
229	Pyraclostrobin	9.06	388	194	163	17	35	Positive
230	Pyridaben	11.01	365	309	147	19	33	Positive
231	Pyridalyl	11.79	490	109	183	15	75	Positive
232	Pyridaphenthion	8.11	341	189	205	29	31	Positive
233	Pyridate	11.24	379	207	351	25	15	Positive
234	Pyrimethanil	7.23	200	107	183	33	33	Positive
235	Pyriofenone	9.39	366	209	184	41	17	Positive
236	Pyriproxyfen	10.11	32	96	185	21	33	Positive
237	Quinalphos	8.70	299	163	243	31	15	Positive
238	Quinoclamine	5.54	208	105	89	33	55	Positive
239	Quinoxyfen	10.19	308	197	162	45	61	Positive
240	Quizalofop	8.32	345	299	244	27	37	Positive
241	Quizalofop-ethyl	9.75	373	299	271	27	35	Positive
242	Rotenone	8.45	395	213	192	31	33	Positive
243	Simazine	5.94	202	132	124	27	27	Positive
244	Spinetoram	9.62	748	142	98	23	51	Positive
245	Spinosym A	9.16	732	142	98	35	97	Positive
246	Spinosyn D	9.50	746	142	98	35	73	Positive
247	Spirodiclofen	10.84	411	313	71	17	35	Positive
248	Spiromesifen	10.67	371	273	255	17	33	Positive
249	Spirotetramat	8.31	374	302	330	25	21	Positive
250	Spiroxamine	7.75	298	144	100	29	45	Positive
251	Sulfoxaflor	4.95	295	174	154	27	47	Positive
252	Tau-fluvalinate	11.27	503	208	181	17	49	Positive
253	Tebuconazole	9.01	308	70	125	53	53	Positive
254	Tebufenozide	8.92	353	297	133	13	27	Positive
255	Tebufenpyrad	10.07	334	145	147	37	35	Positive
256	Terflubenzuron	10.07	379	339	196	-16	-32	Negative
257	Terbutryn	8.08	242	186	91	27	37	Positive
258	Terbutylazine	7.80	230	174	104	23	45	Positive
259	Tetraconazole	8.53	372	159	123	41	87	Positive

No.	Name	t_R (min)	Precursor (m/z)	Product ion 1 (m/z)	Product ion 2 (m/z)	CE 1 (eV)	CE 2 (eV)	Polarity
260	Thiabendazole	4.47	202	175	131	37	45	Positive
261	Thiacloprid	4.94	253	126	90	29	53	Positive
262	Thiamethoxam	4.12	292	211	181	19	33	Positive
263	Thiodicarb	6.00	355	88	108	33	21	Positive
264	Tolclofos methyl	9.15	302	269	125	23	23	Positive
265	Tolfenpyrad	10.02	385	197	154	35	61	Positive
266	Triadimefon	8.13	294	197	225	21	19	Positive
267	Triallate	10.51	304	143	86	41	21	Positive
268	Triazophos	8.14	314	162	119	25	53	Positive
269	Trichlorfon	4.80	257	109	221	23	15	Positive
270	Triclocarban	9.60	315	127	162	45	27	Positive
271	Tricyclazone	5.10	190	163	136	31	39	Positive
272	Trifloxystrobin	9.72	409	186	145	25	69	Positive
273	Triflumizole	9.87	346	278	73	15	21	Positive
274	Triflumuron	9.24	357	154	85	-18	-60	Negative
275	Triticonazole	8.34	318	70	125	55	59	Positive
276	Tritosulfuron	7.19	446	195	221	19	25	Positive
277	Vinclozolin	9.34	286	242	194	31	43	Positive
278	XMC I	6.12	180	123	95	17	29	Positive
279	XMC II	6.36	180	123	95	17	29	Positive
280	XMC III	6.50	180	123	95	17	29	Positive
281	Zoxamide	9.15	336	187	159	31	57	Positive

APPENDIX II: RELATIVE INSTRUMENTAL RESPONSES

Table 1. Relative instrumental response at a concentration level of 0.01 mg/L in **tomato** extract.

Compound	Relative area (1,5µL)	Relative area (2,5µL)	Relative area (5µL)
2,4-D	32%	49%	100%
8-Quinolinol	37%	54%	100%
Acephate	59%	71%	100%
Acetamiprid	45%	62%	100%
Acrinathrin	71%	70%	100%
Alachlor	43%	64%	100%
Albendazole	42%	58%	100%
Aldicarb	37%	57%	100%
Aldicarb sulfone	49%	67%	100%
Ametoctradin	43%	60%	100%
Anilofos	39%	56%	100%
Atrazine	37%	56%	100%
Avermectin_b1a	27%	60%	100%
Avermectin_b1b	30%	59%	100%
Azinphos_methyl	34%	55%	100%
Azinphos-ethyl	35%	57%	100%
Azoxystrobin	37%	56%	100%
BAC10	41%	56%	100%
BAC8	40%	57%	100%
Benalaxyl	36%	55%	100%
Bendiocarb	40%	57%	100%
Benzovindiflupyr	37%	55%	100%
Bifenazate	35%	56%	100%
Bifenthrin	63%	68%	100%
Bitertanol	33%	52%	100%
Bixafen	37%	59%	100%
Boscalid	35%	51%	100%
Bromacil	39%	58%	100%
Bromuconazole_I	37%	54%	100%
Bromuconazole_II	40%	60%	100%
Bupirimate	38%	56%	100%
Buprofezin	39%	59%	100%
Butoxycarboxim	56%	68%	100%
Carbaryl	39%	56%	100%
Carbendazim	65%	78%	100%
carbendazim d3	69%	78%	100%
Carbofuran	28%	55%	100%

Chlorantraniliprole	37%	55%	100%
Chlorbromuron	35%	54%	100%
Chlorfenvinphos	35%	55%	100%
Chlorfluazuron	68%	69%	100%
Chloridazon	54%	70%	100%
Chlorotoluron	38%	56%	100%
Chloroxuron	36%	54%	100%
Chlorpyrifos methyl	43%	54%	100%
Chlorpyriphos	45%	61%	100%
Chromafenozide	36%	56%	100%
Clofentezine	78%	62%	100%
Clomazone	33%	55%	100%
Clopyralid	48%	56%	100%
Coumaphos	37%	58%	100%
Cyazofamid	43%	62%	100%
Cyflufenamid	37%	57%	100%
Cyhalofop-butyl	46%	59%	100%
Cymoxanil	42%	58%	100%
Cyproconazole I	37%	55%	100%
Cyproconazole II	37%	56%	100%
Cyprodinil	38%	57%	100%
Cyromazine I	95%	69%	100%
Cyromazine II	127%	85%	100%
Dazomet	113%	97%	100%
DEET	42%	59%	100%
Deltamethrin	66%	66%	100%
Demeton-S-methylsulfone	53%	68%	100%
Demeton-S-methylsulfoxide	50%	67%	100%
Desethylterbuthylazine	38%	57%	100%
Diazinon	37%	57%	100%
Dichlorvos	36%	56%	100%
Dichlorvos d6	35%	55%	100%
Dicrotophos	48%	63%	100%
Diethofencarb	36%	56%	100%
Difenoconazole	42%	59%	100%
Difenoxuron	38%	55%	100%
Diflubenzuron	31%	50%	100%
Dimethoate	49%	67%	100%
Dimethoate-d6	51%	70%	100%
Dimethomorph I	34%	53%	100%
Dimethomorph II	33%	51%	100%
Dimethylvinphos-Z	35%	54%	100%
Diniconazole	40%	56%	100%
Dinotefuran	70%	81%	100%
Dithianon	81%	68%	100%
Diuron	36%	55%	100%

Dodine	51%	67%	100%
Edifenphos	36%	56%	100%
emamectin b1a	41%	59%	100%
emamectin b1b	46%	63%	100%
EPN	89%	55%	100%
Epoxiconazole	37%	56%	100%
Ethiofencarb	46%	61%	100%
Ethion	44%	60%	100%
Ethiprole	30%	48%	100%
Ethirimol	45%	62%	100%
Ethoprophos	40%	65%	100%
Etofenprox	66%	69%	100%
Etoxazole	60%	61%	100%
Famoxadone	50%	65%	100%
Fenamidone	32%	50%	100%
Fenamiphos	39%	60%	100%
Fenamiphos - sulfone	35%	52%	100%
Fenamiphos - sulfoxide	37%	55%	100%
Fenarimol	35%	50%	100%
Fenazaquin	65%	70%	100%
Fenbendazole	38%	57%	100%
Fenbuconazole	43%	58%	100%
fenhexamid	34%	53%	100%
Fenobucarb	36%	56%	100%
Fenoxycarb	35%	57%	100%
Fenpicoxamid	37%	62%	100%
Fenpropathrin	45%	61%	100%
Fenpropidin	41%	59%	100%
Fenpropimorph	37%	56%	100%
Fenpyrazamine	36%	54%	100%
Fenpyroximate-E	47%	60%	100%
Fensulfothion	36%	53%	100%
Fenthion	46%	58%	100%
Fenthion sulfone	35%	52%	100%
Fenthion sulfoxide	36%	54%	100%
Fenuron	43%	60%	100%
Fipronil	47%	63%	100%
Flazasulfuron	46%	55%	100%
Flonicamid	46%	61%	100%
Fluacrypyrim	38%	57%	100%
Fluazifop-P	34%	52%	100%
Flubendiamide	44%	54%	100%
Flucythrinate	63%	70%	100%
Fludioxonil	38%	56%	100%
Fluensulfone	40%	52%	100%
Flufenacet	41%	62%	100%
Flufenoxuron	63%	64%	100%

Fluometuron	38%	58%	100%
Fluopicolide	35%	55%	100%
Fluopyram	36%	55%	100%
Fluquinconazole	39%	55%	100%
Flusilazole	43%	61%	100%
Flutriafol	37%	54%	100%
Fluxapyroxad	36%	55%	100%
Formetanate hydrochloride	48%	62%	100%
Fosthiazate	38%	56%	100%
Haloxyfop	35%	54%	100%
Hexaconazole	39%	57%	100%
Hexaflumuron	69%	57%	100%
Hexythiazox	47%	63%	100%
Imazalil	44%	60%	100%
Imidacloprid	42%	62%	100%
Indoxacarb	41%	58%	100%
Ioxynil	37%	52%	100%
Iprodione	77%	60%	100%
Iprovalicarb	36%	55%	100%
Isocarbophos	20%	59%	100%
Isofenfos methyl	33%	59%	100%
Isoprocarb	35%	58%	100%
Isoprothiolane	37%	56%	100%
Isoproturon	38%	57%	100%
Kresoxim methyl	39%	57%	100%
Lenacil	35%	56%	100%
Linuron	37%	57%	100%
Lufenuron	49%	63%	100%
Malathion	35%	54%	100%
Malathion-d10	36%	55%	100%
Mandipropamid	40%	58%	100%
Mebendazole	35%	52%	100%
Mepanipyrim	35%	54%	100%
Meptyldinocap	42%	54%	100%
Metaflumizone-E	69%	71%	100%
Metaflumizone-Z	44%	56%	100%
Metalaxyl	43%	59%	100%
Metamitron	39%	67%	100%
Metconazole	39%	56%	100%
Methamidophos	44%	60%	100%
Methidathion	41%	58%	100%
Methiocarb	36%	57%	100%
Methiocarb sulfone	54%	69%	100%
Methiocarb sulfoxide	50%	67%	100%
Methomyl	46%	66%	100%
Methoxyfenozide	34%	55%	100%

Metobromuron	36%	56%	100%
Metolachlor	38%	57%	100%
Metolcarb	34%	54%	100%
Metrafenone	38%	57%	100%
Monocrotophos	52%	67%	100%
Monolinuron	36%	58%	100%
Monuron	39%	57%	100%
Myclobutanyl	38%	57%	100%
Neburon	38%	58%	100%
Nitenpyram	64%	74%	100%
Novaluron	59%	62%	100%
Omethoate	55%	69%	100%
Orthosulfamuron	39%	49%	100%
Oxadiargyl	40%	56%	100%
Oxadixyl	42%	58%	100%
Oxamyl	53%	68%	100%
Oxasulfuron	37%	53%	100%
Oxathiapipronil	34%	54%	100%
Oxfendazole	36%	53%	100%
Oxyfluorfen	69%	53%	100%
Paclobutrazol	34%	52%	100%
Penconazole	41%	60%	100%
Pencycuron	38%	56%	100%
Pendimethalin	42%	59%	100%
Penflufen	36%	56%	100%
Penthiopyrad	35%	57%	100%
Phenthoate	37%	57%	100%
Phosalone	38%	55%	100%
Phosmet	36%	54%	100%
Phoxim	40%	58%	100%
Pirimicarb	32%	44%	100%
Pirimicarb desmethyl	56%	73%	100%
Pirimiphos-methyl	37%	57%	100%
Prochloraz	40%	57%	100%
Profenofos	38%	57%	100%
Promecarb	36%	57%	100%
Prometryn	37%	56%	100%
Propamocarb	49%	64%	100%
Propaquizafop	42%	61%	100%
Propargite	63%	75%	100%
Propazine	37%	57%	100%
Propiconazole I	51%	63%	100%
Propiconazole II	44%	49%	100%
Propoxur	39%	57%	100%
Propyzamide	36%	52%	100%
Proquinazid	42%	58%	100%
Prosulfocarb	36%	57%	100%

Prothioconazole	41%	70%	100%
Prothiofos	95%	63%	100%
Pymetrozine	63%	73%	100%
Pyraclostrobin	40%	58%	100%
Pyridaben	53%	61%	100%
Pyridalyl	59%	62%	100%
Pyridaphenthion	34%	53%	100%
Pyridate	59%	64%	100%
Pyrimethanil	34%	51%	100%
Pyriofenone	34%	54%	100%
Pyriproxyfen	44%	59%	100%
Quinalphos	39%	61%	100%
Quinoclamine	40%	58%	100%
Quinoxyfen	48%	58%	100%
Quizalofop	36%	52%	100%
Quizalofop-ethyl	39%	58%	100%
Rotenone	36%	54%	100%
Simazine	39%	58%	100%
Spinetoram	39%	59%	100%
Spinosyn A	39%	60%	100%
Spinosyn D	38%	58%	100%
Spirodiclofen	55%	62%	100%
Spiromesifen	43%	61%	100%
Spirotetramat	30%	49%	100%
Spiroxamine	38%	55%	100%
Sulfoxaflor	47%	61%	100%
Tau-Fluvalinate	63%	65%	100%
Tebuconazole	38%	56%	100%
Tebufenozide	35%	56%	100%
Tebufenpyrad	38%	56%	100%
Teflubenzuron	34%	57%	100%
Terbutryn	40%	60%	100%
Terbutylazine	39%	58%	100%
Tetraconazole	43%	62%	100%
Thiabendazole	59%	73%	100%
Thiacloprid	41%	59%	100%
Thiamethoxam	57%	74%	100%
Thiobencarb	35%	57%	100%
Tolclofos methyl	46%	58%	100%
Tolfenpyrad	47%	61%	100%
Triadimefon	37%	56%	100%
Triallate	49%	62%	100%
Triazophos	37%	55%	100%
Trichlorfon	43%	61%	100%
Triclocarban	48%	61%	100%
Tricyclazole	45%	60%	100%
Trifloxystrobin	39%	58%	100%

Triflumizole	51%	64%	100%
Triflumuron	34%	55%	100%
Triticonazole	36%	54%	100%
Tritosulfuron	38%	52%	100%
XMC I	35%	56%	100%
XMC II	36%	56%	100%
XMC III	35%	57%	100%
Zoxamide	36%	54%	100%

Table 2. Relative instrumental response at a concentration level of 0.01 mg/L in **onion** extract.

Compound	Relative area (1,5µL)	Relative area (2,5µL)	Relative area (5µL)
2,4-D	25%	43%	100%
8-Quinolinol	42%	62%	100%
Acephate	36%	56%	100%
Acetamiprid	35%	56%	100%
Acrinathrin	41%	52%	100%
Alachlor	46%	66%	100%
Albendazole	54%	78%	100%
Aldicarb	40%	62%	100%
Aldicarb sulfone	33%	54%	100%
Ametoctradin	43%	58%	100%
Anilofos	37%	59%	100%
Atrazine	52%	72%	100%
Avermectin_b1a	35%	57%	100%
Avermectin_b1b	34%	33%	100%
Azinphos_methyl	46%	71%	100%
Azinphos-ethyl	55%	75%	100%
Azoxystrobin	44%	64%	100%
BAC10	43%	65%	100%
BAC8	38%	59%	100%
Benalaxyl	37%	56%	100%
Bendiocarb	43%	63%	100%
Benzovindiflupyr	40%	62%	100%
Bifenazate	46%	69%	100%
Bifenthrin	49%	69%	100%

Bitertanol	31%	57%	100%
Bixafen	44%	62%	100%
Boscalid	41%	66%	100%
Bromacil	47%	70%	100%
Bromuconazole_I	46%	64%	100%
Bromuconazole_II	43%	62%	100%
Bupirimate	41%	62%	100%
Buprofezin	36%	56%	100%
Butoxycarboxim	32%	53%	100%
Carbaryl	42%	63%	100%
Carbendazim	36%	56%	100%
carbendazim d3	37%	56%	100%
Carbofuran	39%	60%	100%
Chlorantraniliprole	41%	61%	100%
Chlorbromuron	43%	66%	100%
Chlorfenvinphos	38%	57%	100%
Chlorfluazuron	40%	53%	100%
Chloridazon	37%	58%	100%
Chlorotoluron	47%	71%	100%
Chloroxuron	48%	68%	100%
Chlorpyrifos methyl	34%	53%	100%
Chlorpyriphos	38%	57%	100%
Chromafenozide	43%	64%	100%
Clofentezine	46%	65%	100%
Clomazone	51%	72%	100%
Clopyralid	32%	47%	100%
Coumaphos	36%	57%	100%
Cyazofamid	46%	65%	100%
Cyflufenamid	53%	64%	100%
Cyhalofop-butyl	42%	56%	100%
Cymoxanil	42%	64%	100%
Cyproconazole I	46%	63%	100%
Cyproconazole II	43%	70%	100%
Cyprodinil	43%	49%	100%
Cyromazine I	89%	97%	100%
Cyromazine II	83%	72%	100%
Dazomet	80%	87%	100%
DEET	52%	73%	100%
Deltamethrin	39%	58%	100%
Demeton-S-methylsulfone	33%	53%	100%
Demeton-S-methylsulfoxide	34%	56%	100%
Desethylterbuthylazine	41%	61%	100%
Diazinon	40%	63%	100%
Dichlorvos	38%	59%	100%
Dichlorvos d6	38%	62%	100%
Dicrotophos	33%	52%	100%

Diethofencarb	54%	75%	100%
Difenoconazole	42%	60%	100%
Difenoxuron	47%	66%	100%
Diflubenzuron	25%	52%	100%
Dimethoate	40%	62%	100%
Dimethoate-d6	39%	60%	100%
Dimethomorph I	36%	60%	100%
Dimethomorph II	38%	58%	100%
Dimethylvinphos-Z	43%	64%	100%
Diniconazole	35%	51%	100%
Dinotefuran	34%	56%	100%
Dithianon	20%	20%	100%
Diuron	61%	84%	100%
Dodine	63%	70%	100%
Edifenphos	38%	58%	100%
emamectin b1a	34%	51%	100%
emamectin b1b	38%	53%	100%
EPN	32%	49%	100%
Epoxiconazole	41%	59%	100%
Ethiofencarb	49%	66%	100%
Ethion	37%	57%	100%
Ethiprole	44%	64%	100%
Ethirimol	41%	62%	100%
Ethoprophos	43%	65%	100%
Etofenprox	50%	62%	100%
Etoxazole	67%	76%	100%
Famoxadone	48%	56%	100%
Fenamidone	42%	60%	100%
Fenamiphos	38%	58%	100%
Fenamiphos - sulfone	38%	59%	100%
Fenamiphos - sulfoxide	40%	60%	100%
Fenarimol	33%	55%	100%
Fenazaquin	53%	70%	100%
Fenbendazole	45%	67%	100%
Fenbuconazole	34%	58%	100%
fenhexamid	37%	57%	100%
Fenobucarb	44%	68%	100%
Fenoxycarb	37%	58%	100%
Fenpicoxamid	49%	67%	100%
Fenpropathrin	41%	59%	100%
Fenpropidin	46%	68%	100%
Fenpropimorph	42%	63%	100%
Fenpyrazamine	37%	58%	100%
Fenpyroximate-E	38%	55%	100%
Fensulfothion	44%	67%	100%
Fensulfothion-oxon sulfone	45%	65%	100%

Fenthion	39%	60%	100%
Fenthion sulfone	37%	58%	100%
Fenthion sulfoxide	42%	63%	100%
Fenuron	36%	55%	100%
Fipronil	42%	66%	100%
Flazasulfuron	48%	70%	100%
Flonicamid	32%	51%	100%
Fluacrypyrim	38%	59%	100%
Fluazifop-P	35%	56%	100%
Flubendiamide	26%	53%	100%
Flucythrinate	54%	66%	100%
Fludioxonil	50%	65%	100%
Fluensulfone	56%	73%	100%
Flufenacet	48%	72%	100%
Flufenoxuron	38%	57%	100%
Fluometuron	50%	70%	100%
Fluopicolide	50%	67%	100%
Fluopyram	42%	61%	100%
Fluquinconazole	36%	53%	100%
Flusilazole	41%	60%	100%
Flutriafol	42%	63%	100%
Fluxapyroxad	50%	69%	100%
Formetanate hydrochloride	34%	53%	100%
Fosthiazate	40%	60%	100%
Haloxyfop	38%	60%	100%
Hexaconazole	38%	53%	100%
Hexaflumuron	32%	53%	100%
Hexythiazox	36%	54%	100%
Imazalil	39%	58%	100%
Imidacloprid	27%	47%	100%
Indoxacarb	36%	55%	100%
Ioxynil	30%	51%	100%
Iprodione	29%	48%	100%
Iprovalicarb	37%	57%	100%
Isocarbophos	62%	90%	100%
Isofenfos methyl	44%	68%	100%
Isoprocarb	44%	65%	100%
Isoprothiolane	46%	64%	100%
Isoproturon	52%	74%	100%
Kresoxim methyl	41%	57%	100%
Lenacil	49%	71%	100%
Linuron	50%	72%	100%
Lufenuron	26%	46%	100%
Malathion	48%	68%	100%
Malathion-d10	45%	67%	100%
Mandipropamid	41%	64%	100%

Mebendazole	35%	57%	100%
Mepanipyrim	40%	60%	100%
Meptyldinocap	28%	46%	100%
Metaflumizone-E	48%	70%	100%
Metaflumizone-Z	28%	43%	100%
Metalaxyl	65%	57%	100%
Metamitron	26%	53%	100%
Metconazole	39%	56%	100%
Methamidophos	33%	53%	100%
Methidathion	50%	68%	100%
Methiocarb	47%	67%	100%
Methiocarb sulfone	41%	61%	100%
Methiocarb sulfoxide	35%	56%	100%
Methomyl	35%	57%	100%
Methoxyfenozide	43%	61%	100%
Metobromuron	49%	74%	100%
Metolachlor	40%	62%	100%
Metolcarb	37%	57%	100%
Metrafenone	40%	61%	100%
Monocrotophos	33%	55%	100%
Monolinuron	40%	62%	100%
Monuron	52%	73%	100%
Myclobutanyl	38%	59%	100%
Neburon	41%	62%	100%
Nitenpyram	32%	53%	100%
Novaluron	38%	51%	100%
Omethoate	34%	53%	100%
Orthosulfamuron	33%	62%	100%
Oxadiargyl	38%	58%	100%
Oxadixyl	41%	63%	100%
Oxamyl	32%	55%	100%
Oxasulfuron	37%	58%	100%
Oxathiapipronil	42%	64%	100%
Oxfendazole	35%	57%	100%
Oxyfluorfen	62%	58%	100%
Paclobutrazol	42%	65%	100%
Penconazole	42%	62%	100%
Pencycuron	40%	61%	100%
Pendimethalin	37%	58%	100%
Penflufen	36%	55%	100%
Penthiopyrad	42%	63%	100%
Phenthoate	41%	61%	100%
Phosalone	37%	59%	100%
Phosmet	45%	66%	100%
Phoxim	40%	62%	100%
Pirimicarb	44%	62%	100%
Pirimicarb desmethyl	47%	63%	100%

Pirimiphos-methyl	36%	60%	100%
Prochloraz	37%	56%	100%
Profenofos	38%	58%	100%
Promecarb	47%	68%	100%
Prometryn	43%	61%	100%
Propamocarb	32%	53%	100%
Propaquizafop	38%	56%	100%
Propargite	46%	58%	100%
Propazine	54%	71%	100%
Propiconazole I	41%	73%	100%
Propiconazole II	40%	69%	100%
Propoxur	44%	63%	100%
Propyzamide	42%	84%	100%
Proquinazid	40%	59%	100%
Prosulfocarb	38%	57%	100%
Prothioconazole	27%	50%	100%
Prothiofos	37%	52%	100%
Pymetrozine	36%	57%	100%
Pyraclostrobin	41%	59%	100%
Pyridaben	37%	53%	100%
Pyridalyl	46%	61%	100%
Pyridaphenthion	41%	59%	100%
Pyridate	43%	53%	100%
Pyrimethanil	40%	63%	100%
Pyriofenone	37%	56%	100%
Pyriproxyfen	39%	59%	100%
Quinalphos	39%	57%	100%
Quinoclamine	46%	68%	100%
Quinoxyfen	42%	61%	100%
Quizalofop	37%	56%	100%
Quizalofop-ethyl	38%	59%	100%
Rotenone	34%	58%	100%
Simazine	47%	68%	100%
Spinetoram	36%	56%	100%
Spinosyn A	37%	58%	100%
Spinosyn D	41%	62%	100%
Spirodiclofen	40%	59%	100%
Spiromesifen	40%	56%	100%
Spirotetramat	35%	56%	100%
Spiroxamine	39%	57%	100%
Sulfoxaflor	62%	73%	100%
Tau-Fluvalinate	41%	58%	100%
Tebuconazole	34%	53%	100%
Tebufenozide	38%	62%	100%
Tebufenpyrad	37%	53%	100%
Teflubenzuron	25%	52%	100%
Terbutryn	45%	64%	100%

Terbutylazine	50%	72%	100%
Tetraconazole	44%	65%	100%
Thiabendazole	36%	57%	100%
Thiacloprid	42%	64%	100%
Thiamethoxam	33%	52%	100%
Thiobencarb	39%	64%	100%
Tolclofos methyl	37%	58%	100%
Tolfenpyrad	38%	51%	100%
Triadimefon	39%	60%	100%
Triallate	45%	64%	100%
Triazophos	42%	64%	100%
Trichlorfon	36%	57%	100%
Triclocarban	39%	47%	100%
Tricyclazole	36%	57%	100%
Trifloxystrobin	41%	60%	100%
Triflumizole	44%	65%	100%
Triflumuron	26%	49%	100%
Triticonazole	39%	60%	100%
Tritosulfuron	55%	51%	100%
XMC I	46%	72%	100%
XMC II	39%	61%	100%
XMC III	40%	62%	100%
Zoxamide	38%	57%	100%

Table 3. Relative instrumental response at a concentration level of 0.01 mg/L in **raisins** extract.

Compound	**Relative area (1,5µL)**	**Relative area (2,5µL)**	**Relative area (5µL)**
2,4-D	28%	51%	100%
8-Quinolinol	31%	54%	100%
Acephate	38%	62%	100%
Acetamiprid	35%	58%	100%
Acrinathrin	42%	56%	100%
Alachlor	37%	53%	100%
Albendazole	42%	61%	100%
Aldicarb	33%	54%	100%
Aldicarb sulfone	33%	55%	100%
Ametoctradin	44%	63%	100%

Anilofos	38%	54%	100%
Atrazine	34%	55%	100%
Avermectin_b1a	33%	52%	100%
Avermectin_b1b	22%	37%	100%
Azinphos_methyl	32%	50%	100%
Azinphos-ethyl	35%	54%	100%
Azoxystrobin	34%	52%	100%
BAC10	38%	54%	100%
BAC8	35%	55%	100%
Benalaxyl	37%	54%	100%
Bendiocarb	33%	55%	100%
Benzovindiflupyr	35%	52%	100%
Bifenazate	96%	78%	100%
Bifenthrin	45%	66%	100%
Bitertanol	31%	54%	100%
Bixafen	34%	54%	100%
Boscalid	33%	50%	100%
Bromacil	33%	53%	100%
Bromuconazole_I	33%	57%	100%
Bromuconazole_II	34%	54%	100%
Bupirimate	36%	54%	100%
Buprofezin	38%	57%	100%
Butoxycarboxim	32%	53%	100%
Carbaryl	32%	53%	100%
Carbendazim	40%	63%	100%
carbendazim d3	40%	64%	100%
Carbofuran	32%	55%	100%
Chlorantraniliprole	28%	50%	100%
Chlorbromuron	34%	53%	100%
Chlorfenvinphos	34%	53%	100%
Chlorfluazuron	36%	59%	100%
Chloridazon	38%	61%	100%
Chlorotoluron	33%	54%	100%
Chloroxuron	34%	52%	100%
Chlorpyrifos methyl	39%	57%	100%
Chlorpyriphos	37%	56%	100%
Chromafenozide	33%	50%	100%
Clofentezine	36%	57%	100%
Clomazone	31%	54%	100%
Clopyralid	29%	51%	100%
Coumaphos	37%	54%	100%
Cyazofamid	37%	60%	100%
Cyflufenamid	37%	73%	100%
Cyhalofop-butyl	36%	54%	100%
Cymoxanil	38%	57%	100%
Cyproconazole I	38%	60%	100%
Cyproconazole II	38%	55%	100%

Cyprodinil	39%	56%	100%
Cyromazine I	87%	97%	100%
Cyromazine II	95%	81%	100%
Dazomet	116%	100%	100%
DEET	37%	56%	100%
Deltamethrin	40%	59%	100%
Demeton-S-methylsulfone	34%	58%	100%
Demeton-S-methylsulfoxide	33%	58%	100%
Desethylterbuthylazine	33%	54%	100%
Diazinon	40%	57%	100%
Dichlorvos	32%	54%	100%
Dichlorvos d6	31%	52%	100%
Dicrotophos	34%	58%	100%
Diethofencarb	34%	55%	100%
Difenoconazole	38%	58%	100%
Difenoxuron	32%	54%	100%
Diflubenzuron	35%	47%	100%
Dimethoate	37%	60%	100%
Dimethoate-d6	38%	60%	100%
Dimethomorph I	30%	50%	100%
Dimethomorph II	27%	47%	100%
Dimethylvinphos-Z	32%	50%	100%
Diniconazole	35%	53%	100%
Dinotefuran	39%	63%	100%
Dithianon	60%	72%	100%
Diuron	32%	55%	100%
Dodine	43%	60%	100%
Edifenphos	36%	55%	100%
emamectin b1a	39%	56%	100%
emamectin b1b	36%	63%	100%
EPN	61%	58%	100%
Epoxiconazole	39%	58%	100%
Ethiofencarb	40%	54%	100%
Ethion	35%	55%	100%
Ethiprole	29%	48%	100%
Ethirimol	35%	58%	100%
Ethoprophos	38%	56%	100%
Etofenprox	51%	67%	100%
Etoxazole	45%	63%	100%
Famoxadone	46%	61%	100%
Fenamidone	30%	50%	100%
Fenamiphos	37%	56%	100%
Fenamiphos - sulfone	31%	51%	100%
Fenamiphos - sulfoxide	30%	50%	100%
Fenarimol	34%	57%	100%
Fenazaquin	51%	67%	100%

Fenbendazole	38%	60%	100%
Fenbuconazole	41%	59%	100%
fenhexamid	31%	44%	100%
Fenobucarb	31%	54%	100%
Fenoxycarb	32%	51%	100%
Fenpicoxamid	28%	43%	100%
Fenpropathrin	38%	54%	100%
Fenpropidin	36%	55%	100%
Fenpropimorph	36%	54%	100%
Fenpyrazamine	34%	54%	100%
Fenpyroximate-E	37%	56%	100%
Fensulfothion	32%	50%	100%
Fensulfothion-oxon sulfone	32%	50%	100%
Fenthion	45%	60%	100%
Fenthion sulfone	32%	51%	100%
Fenthion sulfoxide	30%	51%	100%
Fenuron	36%	57%	100%
Fipronil	42%	54%	100%
Flazasulfuron	37%	51%	100%
Flonicamid	31%	54%	100%
Fluacrypyrim	39%	56%	100%
Fluazifop-P	30%	50%	100%
Flubendiamide	33%	54%	100%
Flucythrinate	35%	60%	100%
Fludioxonil	32%	55%	100%
Fluensulfone	68%	48%	100%
Flufenacet	31%	53%	100%
Flufenoxuron	36%	54%	100%
Fluometuron	32%	54%	100%
Fluopicolide	32%	50%	100%
Fluopyram	34%	52%	100%
Fluquinconazole	33%	57%	100%
Flusilazole	40%	57%	100%
Flutriafol	34%	53%	100%
Fluxapyroxad	33%	53%	100%
Formetanate hydrochloride	33%	56%	100%
Fosthiazate	32%	53%	100%
Haloxyfop	33%	56%	100%
Hexaconazole	40%	55%	100%
Hexaflumuron	38%	56%	100%
Hexythiazox	36%	54%	100%
Imazalil	37%	56%	100%
Imidacloprid	31%	54%	100%
Indoxacarb	34%	54%	100%
Ioxynil	33%	52%	100%

Iprodione	43%	54%	100%
Iprovalicarb	35%	54%	100%
Isocarbophos	32%	49%	100%
Isofenfos methyl	38%	56%	100%
Isoprocarb	34%	54%	100%
Isoprothiolane	35%	56%	100%
Isoproturon	34%	57%	100%
Kresoxim methyl	36%	55%	100%
Lenacil	32%	53%	100%
Linuron	35%	53%	100%
Lufenuron	36%	54%	100%
Malathion	36%	54%	100%
Malathion-d10	33%	50%	100%
Mandipropamid	37%	57%	100%
Mebendazole	31%	51%	100%
Mepanipyrim	33%	54%	100%
Meptyldinocap	35%	53%	100%
Metaflumizone-E	40%	53%	100%
Metaflumizone-Z	20%	41%	100%
Metalaxyl	36%	55%	100%
Metamitron	24%	57%	100%
Metconazole	36%	57%	100%
Methamidophos	33%	55%	100%
Methidathion	35%	54%	100%
Methiocarb	33%	57%	100%
Methiocarb sulfone	39%	61%	100%
Methiocarb sulfoxide	34%	59%	100%
Methomyl	34%	55%	100%
Methoxyfenozide	34%	53%	100%
Metobromuron	31%	54%	100%
Metolachlor	36%	52%	100%
Metolcarb	30%	51%	100%
Metrafenone	38%	56%	100%
Monocrotophos	36%	60%	100%
Monolinuron	31%	51%	100%
Monuron	33%	53%	100%
Myclobutanyl	33%	51%	100%
Neburon	38%	57%	100%
Nitenpyram	32%	58%	100%
Novaluron	28%	53%	100%
Omethoate	33%	56%	100%
Orthosulfamuron	31%	48%	100%
Oxadiargyl	39%	57%	100%
Oxadixyl	33%	54%	100%
Oxamyl	31%	52%	100%
Oxasulfuron	29%	51%	100%
Oxathiapipronil	34%	52%	100%

Oxfendazole	29%	50%	100%
Oxyfluorfen	45%	60%	100%
Paclobutrazol	33%	54%	100%
Penconazole	42%	62%	100%
Pencycuron	37%	58%	100%
Pendimethalin	39%	61%	100%
Penflufen	36%	53%	100%
Penthiopyrad	35%	52%	100%
Phenthoate	34%	53%	100%
Phosalone	35%	53%	100%
Phosmet	32%	52%	100%
Phoxim	38%	58%	100%
Pirimicarb	34%	56%	100%
Pirimicarb desmethyl	37%	59%	100%
Pirimiphos-methyl	40%	56%	100%
Prochloraz	41%	59%	100%
Profenofos	36%	55%	100%
Promecarb	34%	55%	100%
Prometryn	37%	57%	100%
Propamocarb	32%	53%	100%
Propaquizafop	34%	52%	100%
Propargite	40%	57%	100%
Propazine	33%	56%	100%
Propiconazole I	38%	51%	100%
Propiconazole II	41%	46%	100%
Propoxur	31%	54%	100%
Propyzamide	35%	60%	100%
Proquinazid	36%	56%	100%
Prosulfocarb	34%	56%	100%
Prothioconazole	87%	62%	100%
Prothiofos	51%	72%	100%
Pymetrozine	38%	59%	100%
Pyraclostrobin	38%	57%	100%
Pyridaben	38%	56%	100%
Pyridalyl	42%	64%	100%
Pyridaphenthion	31%	49%	100%
Pyridate	39%	56%	100%
Pyrimethanil	32%	54%	100%
Pyriofenone	37%	55%	100%
Pyriproxyfen	49%	70%	100%
Quinalphos	35%	55%	100%
Quinoclamine	34%	55%	100%
Quinoxyfen	40%	62%	100%
Quizalofop	34%	51%	100%
Quizalofop-ethyl	35%	53%	100%
Rotenone	32%	51%	100%
Simazine	33%	55%	100%

Spinetoram	34%	55%	100%
Spinosyn A	36%	54%	100%
Spinosyn D	38%	55%	100%
Spirodiclofen	38%	60%	100%
Spiromesifen	42%	59%	100%
Spirotetramat	30%	50%	100%
Spiroxamine	33%	54%	100%
Sulfoxaflor	31%	55%	100%
Tau-Fluvalinate	40%	61%	100%
Tebuconazole	35%	50%	100%
Tebufenozide	35%	53%	100%
Tebufenpyrad	35%	52%	100%
Teflubenzuron	36%	53%	100%
Terbutryn	36%	54%	100%
Terbutylazine	35%	56%	100%
Tetraconazole	43%	61%	100%
Thiabendazole	45%	69%	100%
Thiacloprid	42%	62%	100%
Thiamethoxam	32%	55%	100%
Thiobencarb	36%	55%	100%
Tolclofos methyl	43%	63%	100%
Tolfenpyrad	32%	46%	100%
Triadimefon	29%	49%	100%
Triallate	22%	47%	100%
Triazophos	35%	56%	100%
Trichlorfon	33%	55%	100%
Triclocarban	34%	48%	100%
Tricyclazole	37%	59%	100%
Trifloxystrobin	39%	56%	100%
Triflumizole	47%	64%	100%
Triflumuron	32%	52%	100%
Triticonazole	37%	54%	100%
Tritosulfuron	32%	47%	100%
XMC I	32%	53%	100%
XMC II	31%	54%	100%
XMC III	31%	53%	100%
Zoxamide	32%	50%	100%