Quantitative analysis of residual agricultural chemicals in food by GC-MS/MS

- Quantitative analysis of pesticides in spinach extract -

Product: JMS-TQ4000GC GC-MS/MS System

Introduction

As "food safety" is recognized as an increasingly important issue on a global scale, many nations have their own regulations on residual agricultural chemicals in food. In Japan, the positive list system, which was enforced at the end of May 2006, stipulates a uniform standard of 10 ppb as a quantity that is considered safe for human health. Under the positive list system, more agricultural chemicals need to be examined, and as a result, techniques capable of accurately and collectively analyzing residual agricultural chemicals in food are in increasing demand. While mass spectrometry (MS) is known for its high detection sensitivity, MS/MS is becoming the mainstream of pesticide analysis for its superior sensitivity and selectivity.
The JMS-TQ4000GC, JEOL's latest GC-MS/MS, has a unique ion storage/ejection mechanism within the MS/MS collision cell and incorporates new firmware to support MS/MS analysis with up to 36,000 transitions. In this work, we performed quantitative analysis of residual agricultural chemicals in spinach extract using a JMS-TQ4000GC.

Experiment

A pesticide standard solution from FUJIFILM Wako Pure Chemical Corporation (PL series) was used that consisted of equal amounts of PL 1, 2, 3, 4, 5, 6, 11, and 12. Afterwards, the solution was diluted to 1, 5, 10, 50 and 100 ppb. PEG 300 was used to protect the pesticides from thermal decomposition in the GC injection liner.
For the sample, 15 g of spinach was processed by using AOAC 2007.01 extraction method, and the resulting extraction solution was mixed with 100 ppb of the standard solution at 9:1. The sample was quantitatively analyzed for 150 pesticides. Table 1 shows the measurement conditions used for the analysis.

GC-MS/MS, JMS-TQ4000GC

Table 1. Measurement conditions

System	JMS-TQ4000GC (JEOL)
Ionization mode	EI+: 70eV, 50µA
GC column	VF-5ms, 30m x 0.25mm, 0.25µm
Oven temp.	50°C (1min)→25°C/min→125°C →10°C/min→300°C
Inlet temp.	250°C
Inlet mode	Splitless, 2µL
He flow	1.0mL/min (Constant Flow)
MS/MS mode	Peak Dependent SRM

Results and discussions

Figure 1 top row shows the data acquired from the original spinach extract while the bottom row shows the data the spinach extraction solution with the pesticides added. MS/MS, with its high mass selectivity, detected agricult chemicals without being affected by contaminants in the spinach extract.

Table 2 shows the quantitative results of 150 pesticides (n=5) and their reproducibility (CV). For most agricultural chemicals, the recovery rate was 70 to 120% and the CV was 10% or less, demonstrating the effectiveness of the TQ4000GC for pesticide analysis.

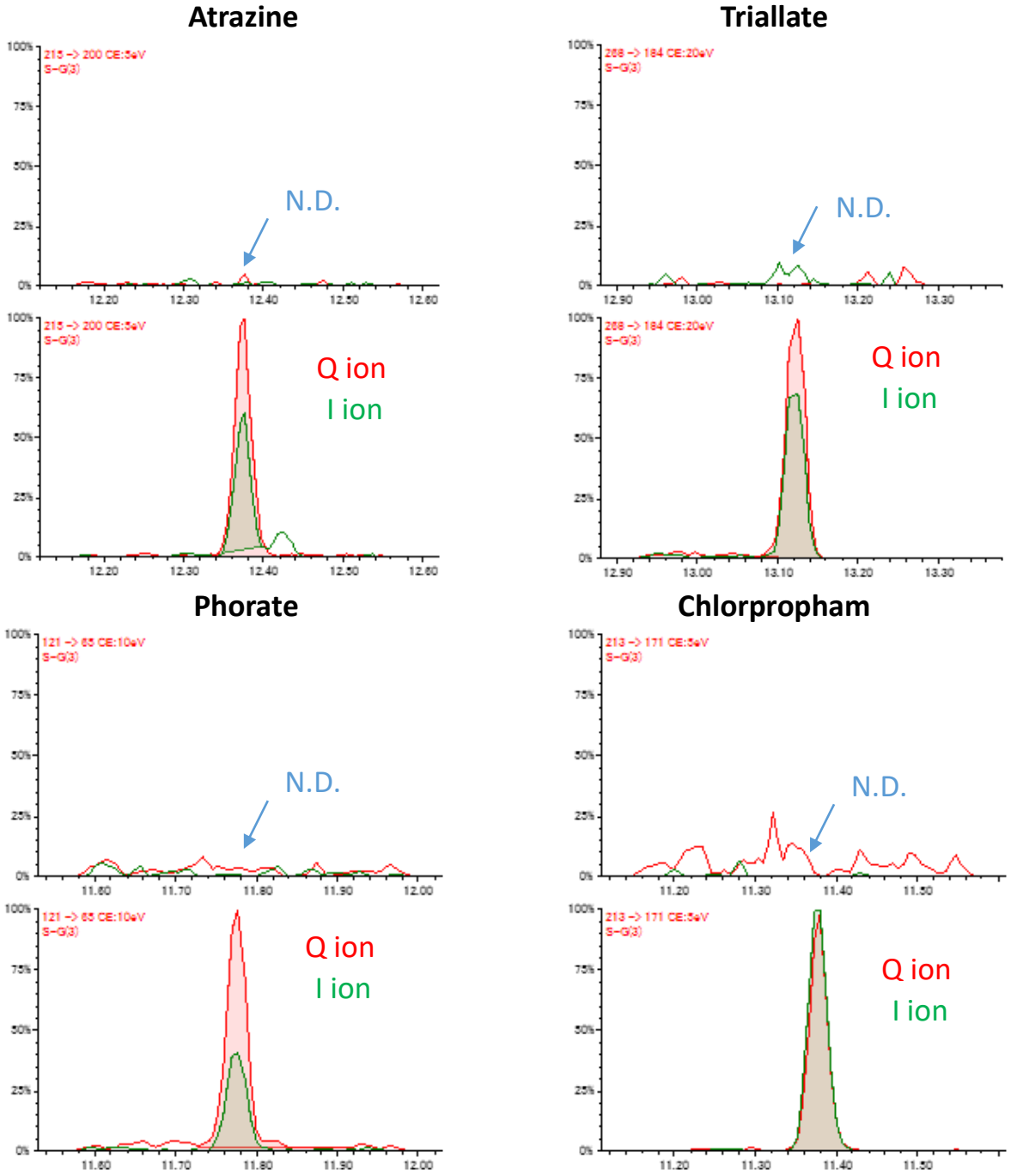

Figure 1. SRM chromatograms
Upper: Spinach extract solution only, lower: 10ppb pesticides in the spinach extract solution

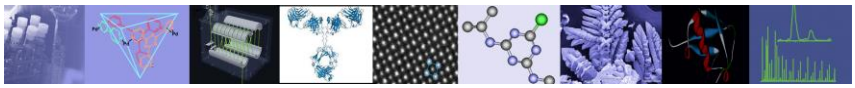

Table 2 Quantitative result 150 pesticides in the spinach extract solution (n=5)

No.	Compound	RT (min)	Quantitative values (ppb)					Ave. (ppb)	CV (%)
			No.1	No.2	No.3	No.4	No.5		
1	Atrazine	12.37	10.0	10.0	9.7	10.4	9.2	9.9	4.4
2	Benthiocarb	14.68	10.1	10.7	11.6	11.5	10.8	10.9	5.8
3	cis-Permethrin	20.68	12.5	12.8	12.8	12.3	12.6	12.6	1.9
4	Diflufenican	18.31	11.7	11.6	12.0	11.2	10.7	11.4	4.3
5	Fenamiphos	16.24	9.1	11.6	10.4	10.9	9.5	10.3	9.8
6	Fenarimol	20.20	11.1	11.1	11.1	11.3	11.1	11.1	0.7
7	Fenpropimorph	14.74	11.0	11.4	10.7	11.8	10.6	11.1	4.6
8	Norflurazon	17.94	10.7	10.2	10.6	10.2	10.7	10.5	2.3
9	Oxadiazon	16.50	10.6	9.9	11.0	10.8	10.3	10.5	4.0
10	Penconazole	15.45	11.7	10.8	10.9	11.3	11.2	11.2	3.0
11	Pendimethalin	15.29	12.9	11.7	12.3	11.9	12.5	12.3	3.7
12	Procymidone	15.70	10.6	10.8	12.4	9.4	9.7	10.6	11.2
13	Spiroxamine 1	13.78	8.6	8.3	8.2	8.6	8.5	8.4	2.1
14	Spiroxamine 2	14.31	9.2	8.7	9.0	9.4	8.5	9.0	3.9
15	Tefluthrine	12.92	10.2	9.9	10.3	10.5	10.1	10.2	2.2
16	Terbufos	12.63	8.3	7.9	7.9	8.7	7.6	8.1	5.0
17	Terbutryn	14.31	10.5	9.6	10.1	10.4	9.7	10.0	4.0
18	trans-Permethrin	20.68	12.5	12.8	12.8	12.3	12.6	12.6	1.9
19	Alachlor	13.84	9.7	9.0	8.9	9.3	8.7	9.1	4.5
20	Buprofezin	16.68	11.2	11.7	11.1	11.9	11.9	11.6	3.2
21	cis-Chlorfenvinphos	15.49	6.3	7.6	7.9	7.6	6.4	7.2	10.4
22	Cyproconazole 1	17.03	12.1	12.4	11.2	9.9	12.2	11.6	9.1
23	Cyproconazole 2	17.03	11.6	11.0	12.0	12.3	11.3	11.7	4.6
24	Difenoconazole 1	23.10	11.3	11.2	11.3	11.0	11.3	11.2	1.4
25	Difenoconazole 2	23.18	11.7	11.1	11.2	11.3	11.4	11.3	2.0
26	Ethion	17.34	10.2	10.6	10.9	10.0	9.9	10.3	4.0
27	Fenitrothion	14.33	8.3	9.0	10.7	9.3	9.1	9.3	9.5
28	Fenthion	14.73	8.9	10.0	8.7	9.4	8.4	9.1	7.1
29	Fluridone	22.18	11.1	12.0	12.0	11.7	11.6	11.7	3.3
30	Hexazinone	18.24	9.5	9.9	10.0	9.5	9.0	9.6	3.9
31	Isofenphos oxon	14.79	10.1	12.8	13.3	10.4	10.6	11.5	12.9
32	Isophenphos	15.43	9.7	8.5	10.0	9.8	10.1	9.6	6.5
33	Isoprothiolane	16.44	11.1	11.2	11.0	10.1	12.4	11.2	7.4
34	Propargite 1	18.31	6.7	7.2	7.4	7.0	7.3	7.1	4.1
35	Propargite 2	18.31	6.9	7.3	7.4	7.2	6.8	7.1	3.9
36	Propiconazole 1	17.93	12.6	12.9	12.2	12.1	12.0	12.4	3.1
37	Propiconazole 2	18.07	13.5	12.4	12.3	12.9	13.0	12.8	4.0
38	Propyzamide	12.73	11.0	10.6	11.1	10.4	10.4	10.7	3.2
39	Pyriproxyfen	19.72	11.0	10.9	10.9	11.1	10.7	10.9	1.3
40	trans-Chlorfenvinphos	15.25	7.6	9.4	8.4	8.5	6.4	8.1	14.1
41	Triadimenol 1	15.70	12.2	10.0	10.5	10.5	10.5	10.7	8.1
42	Triadimenol 2	15.84	12.8	10.6	11.9	10.7	11.0	11.4	8.1
43	Triallate	13.13	7.4	7.9	8.1	8.3	7.4	7.8	5.0
44	Vinclozoline	13.76	7.2	8.0	8.3	7.5	7.6	7.7	5.6
45	Acetamiprid	18.92	10.3	10.9	10.7	10.3	11.5	10.8	4.8
46	Allethrin 1	15.43	10.0	9.5	11.3	10.9	11.7	10.7	8.5
47	Allethrin 2	15.51	9.0	10.5	9.2	9.1	10.3	9.6	7.7
48	Bitertanol 1	20.66	14.1	14.1	14.0	14.1	14.0	14.0	0.5
49	Bitertanol 2	20.76	10.8	11.1	11.0	11.7	11.2	11.2	3.0
50	Bromopropylate	19.00	9.6	10.6	10.7	10.3	9.8	10.2	4.7
51	Chlorobenzilate	17.19	8.7	9.4	10.1	9.4	8.6	9.3	6.9
52	Chlorpyrifos	14.63	8.5	9.4	8.8	9.0	8.6	8.9	4.0
53	Oxyfluorfen	16.59	14.1	12.8	13.6	12.4	11.1	12.8	9.0
54	Parathion	14.80	13.2	14.4	12.5	13.0	13.8	13.4	5.6
55	Pirimiphos methyl	14.24	9.6	9.8	9.5	9.5	9.5	9.6	1.3
56	Propanil	13.67	10.1	10.1	10.6	10.1	10.2	10.2	1.9
57	Pyridaben	20.87	10.7	12.8	13.1	11.5	11.1	11.8	8.9
58	Quinoxyfen	18.00	11.7	11.5	12.1	11.7	11.5	11.7	2.1
59	Simazine	12.29	9.3	10.4	9.5	10.2	10.2	9.9	4.9
60	Tebuconazole	18.38	10.2	10.6	10.5	11.1	10.3	10.5	3.0
61	Triadimefon	14.87	11.1	10.4	10.1	10.6	9.0	10.3	7.6
62	Triazophos	17.65	7.4	9.1	8.5	8.0	7.2	8.0	9.9
63	Ametryn	14.00	10.7	10.1	10.3	10.1	10.4	10.3	2.2
64	Azaconazole	16.83	13.8	13.6	14.5	13.7	13.3	13.8	3.2
65	Bupirimate	16.66	11.0	10.4	11.3	11.1	10.4	10.8	3.8
66	Butachlor	16.01	9.9	9.8	10.6	9.7	9.4	9.9	4.4
67	Chlorthal dimethyl	14.73	9.4	8.9	9.4	8.8	8.5	9.0	4.4
68	Dicloran	12.19	6.8	8.3	8.4	7.6	6.3	7.5	12.1
69	Diethofencarb	14.63	12.3	10.8	11.2	10.9	10.7	11.2	6.0
70	Dimepiperate	15.74	13.3	11.4	13.6	12.4	13.4	12.8	7.0
71	Dimethenamid	13.61	10.0	9.6	10.1	10.4	9.5	9.9	3.6
72	Etoxazole	19.03	11.0	11.1	11.1	10.9	11.2	11.0	0.9
73	Fluacrypyrim	17.38	11.1	10.8	11.0	11.2	10.6	11.0	2.3
74	Lenacil	18.14	10.6	12.3	11.4	11.6	10.6	11.3	6.6
75	Pyriminobac methyl 1	17.96	12.8	12.3	12.5	12.7	12.6	12.6	1.5
76	Pyriminobac methyl 2	12.88	10.8	10.9	11.0	10.4	10.8	10.8	2.1
77	Pyroquilon	19.53	10.3	9.2	9.7	9.7	10.0	9.8	4.2
78	Tetradifon	13.87	7.5	9.3	9.4	8.5	8.1	8.6	9.1
79	Tolclofos-methyl	16.61	9.2	9.2	9.2	9.2	9.1	9.2	0.6
80	Uniconazole P	13.66	11.5	12.4	10.8	11.5	10.6	11.4	6.3
81	Acetochlor	17.83	9.3	8.7	8.8	9.3	8.9	9.0	3.3
82	Benalaxyl	13.57	10.7	9.9	10.3	10.2	9.8	10.2	3.5
83	Benfuresate	11.71	9.6	9.3	9.4	9.7	9.6	9.5	1.6
84	Cadusafos	11.37	8.2	8.3	8.0	8.6	7.9	8.2	3.5
85	Chlorpropham	15.61	8.9	8.5	8.2	9.1	8.9	8.7	4.4
86	Diclocymet 1	15.91	10.4	10.8	10.4	10.9	10.2	10.5	2.9
87	Diclocymet 2	15.40	10.0	10.4	10.8	9.9	10.0	10.2	3.4
88	Dimethametryn	14.49	12.0	10.7	11.7	11.6	11.4	11.5	4.3
89	Esprocarb	21.83	9.3	9.4	9.3	9.7	9.1	9.4	2.5
90	Etofenprox	16.08	12.8	12.6	12.7	12.9	12.4	12.7	1.5
91	Fenothiocarb	13.27	10.4	10.3	10.4	10.7	11.0	10.6	2.9
92	Iprobenfos	16.92	9.6	9.0	10.0	10.0	9.2	9.6	4.7
93	Isoxathion	17.61	6.6	8.0	8.0	6.7	6.9	7.3	9.8
94	Mepronil	14.04	11.4	11.1	11.8	11.6	11.5	11.5	2.2
95	Prometryn	10.85	10.2	9.7	10.0	10.9	9.8	10.1	4.8
96	Propachlor	16.41	9.4	7.6	7.0	8.0	7.5	7.9	11.5
97	Prothiofos	15.99	8.7	9.7	8.9	9.3	9.2	9.1	4.4
98	Pyrifenox 1	12.89	10.2	10.0	10.6	10.5	10.6	10.4	2.3
99	Pyrimethanil	13.94	9.4	9.4	9.6	10.5	8.9	9.6	6.0
100	Simetryn	13.06	11.0	10.6	9.4	10.2	10.7	10.4	6.0
101	Terbacil	14.82	8.7	10.0	9.9	10.2	9.2	9.6	6.6
102	Tetraconazole	18.31	11.9	11.6	11.7	10.9	13.4	11.9	7.7
103	Thenylchlor	16.58	7.1	8.1	8.8	8.0	7.8	8.0	7.3
104	Tribufos	16.66	9.0	10.4	9.7	9.8	8.3	9.4	8.4
105	Tricyclazole	15.72	4.4	6.9	6.3	5.4	4.7	5.5	18.8
106	Zoxamide (decomposed)	13.40	10.5	11.1	11.0	10.3	9.6	10.5	5.7
107	Benoxacor	14.44	4.2	4.7	5.0	4.5	3.8	4.4	10.1
108	Bromacil	13.70	6.6	8.1	8.1	8.4	7.9	7.8	9.0
109	Bromobutide	16.17	11.7	9.7	10.5	11.8	10.2	10.8	8.7
110	Butamifos	13.56	10.3	12.0	11.7	11.0	10.9	11.2	6.3
111	Dichlofenthion	15.12	9.7	9.3	9.5	10.2	9.1	9.6	4.6
112	Diphenamid	16.42	12.2	11.5	12.2	11.9	12.1	12.0	2.3
113	Hexaconazole	14.00	10.0	11.6	11.4	9.9	11.4	10.9	7.7
114	Mefenoxam	16.33	16.3	15.5	17.4	16.6	16.1	16.4	4.4
115	Napropamide	17.40	10.6	10.6	10.8	10.5	10.1	10.5	2.5
116	Oxadixyl	16.07	9.2	10.9	10.2	9.6	9.1	9.8	7.5
117	Paclobutrazol	19.31	11.8	12.0	12.8	12.3	12.1	12.2	3.1
118	Phenothrin 1	19.42	13.8	10.0	11.1	12.0	10.5	11.5	13.3
119	Phenothrin 2	18.98	11.5	11.2	11.0	11.0	11.2	11.2	1.8
120	Piperophos	12.94	9.9	10.0	11.3	10.9	10.5	10.5	5.5
121	Prohydrojasmon 1	13.23	8.8	8.5	8.4	8.9	8.1	8.5	3.8
122	Prohydrojasmon 2	12.42	11.8	12.2	11.2	14.5	12.2	12.4	10.3
123	Propazine	18.63	9.7	8.5	9.3	9.8	8.8	9.2	6.0
124	Pyributicarb	15.51	13.0	12.7	13.0	13.1	12.9	12.9	1.1
125	Pyrifenox 2	15.63	10.6	9.9	11.1	10.0	9.7	10.3	5.5
126	Quinalphos	19.16	10.1	11.1	11.8	11.6	10.1	11.0	7.3
127	Tebufenpyrad	24.05	11.1	10.7	11.4	10.8	10.9	11.0	2.7
128	Tolfenpyrad	14.78	11.5	11.5	11.7	11.5	11.4	11.5	0.9
129	Aldrin	16.26	7.4	8.5	9.7	8.5	9.2	8.7	10.0
130	cis-Chlordane	14.97	8.5	9.4	9.6	8.5	9.3	9.1	5.7
131	Dicofol	16.78	11.7	10.7	10.6	10.9	10.8	11.0	3.8
132	Dieldrin	17.19	8.2	8.3	10.4	7.4	10.0	8.8	14.4
133	Endrin	14.07	8.7	10.0	10.7	10.6	8.5	9.7	10.7
134	Heptachlor	16.02	5.9	6.8	6.6	6.8	6.0	6.4	6.7
135	trans-Chlordane	14.40	9.9	9.0	9.7	9.7	9.3	9.5	3.8
136	1-Naphthylacetamide	15.87	14.4	13.2	14.3	13.6	14.1	13.9	3.6
137	Bromophos ethyl	16.80	8.9	8.6	9.5	8.8	8.6	8.9	4.1
138	Carboxin	15.98	3.5	3.6	3.4	3.7	3.5	3.5	3.4
139	Chlorbenside	16.42	10.0	9.7	9.5	10.0	9.8	9.8	1.9
140	Chlorofenson	24.99	6.8	8.6	8.7	8.2	7.4	7.9	10.6
141	clomazone	12.47	8.0	8.3	8.9	8.9	7.9	8.4	5.7
142	Disulfoton	12.98	7.5	7.4	7.3	8.1	7.3	7.5	4.6
143	Epoxiconazole	18.61	11.4	11.3	11.8	11.1	11.3	11.4	2.1
144	Ethofumesate	14.37	10.2	10.0	10.2	10.5	9.3	10.0	4.6
145	Fenamidone	19.17	11.8	11.1	10.9	12.1	11.1	11.4	4.7
146	Flutriafol	16.28	12.6	11.3	11.7	11.2	11.5	11.6	4.7
147	Isazophos	12.96	10.1	9.4	9.6	10.4	9.4	9.8	4.6
148	Phorate	11.79	8.3	8.5	7.5	8.3	8.4	8.2	4.9
149	Picolinafen	18.97	12.9	11.5	11.8	11.2	12.6	12.0	6.1
150	Propaphos	15.89	10.8	11.2	11.7	10.7	10.9	11.1	3.5

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