

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

- Quantitative analysis of pesticides in carrot 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 carrot 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.

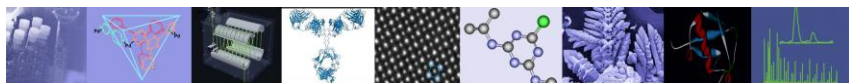
For the sample, 15 g of carrots was processed by using the AOAC 2007.01 extraction method, and the resulting extraction solution was mixed with 100 ppb of the standard solution at 9:1. The sample was quantitatively analyzed for 150 pesticides. Table 1 shows the measurement conditions used for the analysis.

Table 1. Measurement conditions

System	JMS-TQ4000GC (JEOL)
Ionization mode	El+: 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



GC-MS/MS, JMS-TQ4000GC



Results and discussions

Figure 1 top row shows the data acquired from the original carrot extract while the bottom row shows the data for the carrot extraction solution with the pesticides added. MS/MS, with its high mass selectivity, detected agricultural chemicals without being affected by contaminants in the carrot extract. Table 2 shows the quantitative results of pesticides (n=5) and their reproducibility (CV). For most agricultural chemicals, the recovery rate was 70 to 120% the CV was 10% or less, demonstrating the effectiveness of the JMS-TQ4000GC for pesticide analysis.

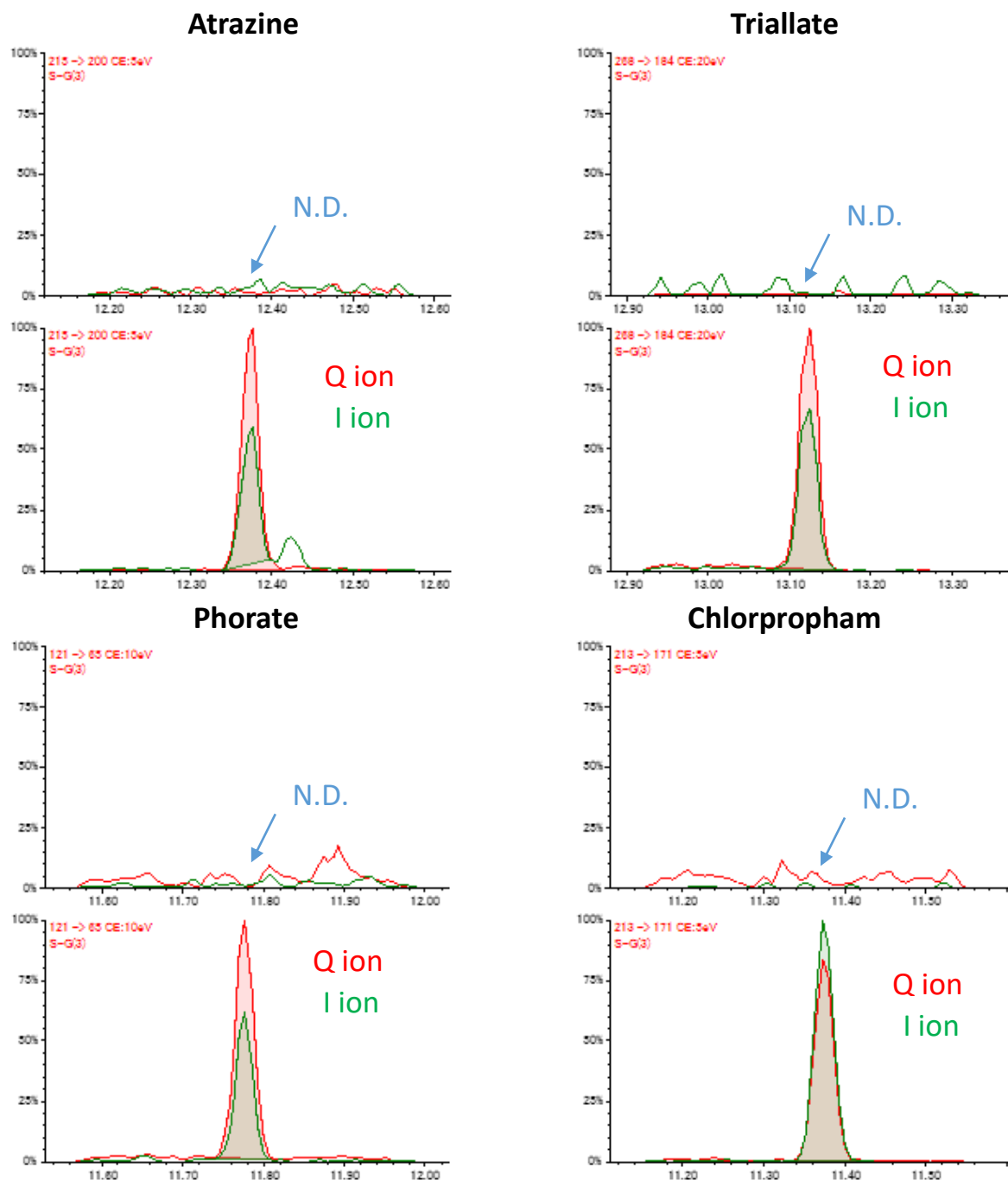


Figure 1. SRM chromatograms

Top row: Carrot extract solution only; bottom row: 10 ppb pesticides in carrot extract solution

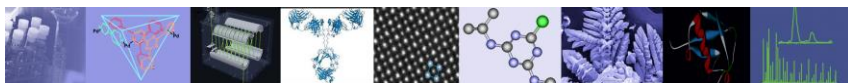


Table 2. Quantitative results of 150 pesticides in carrot extract solution (n=5)

No.	Compound	min	Quantitative value (ppb)					Ave. (ppb)	CV (%)
			No.1	No.2	No.3	No.4	No.5		
1	Atrazine	12.37	9.1	10.1	9.6	9.8	9.1	9.5	4.5
2	Benthiocarb	14.68	10.7	10.9	11.8	11.2	10.9	11.1	4.0
3	cis-Permethrin	20.68	11.0	10.8	11.5	11.2	11.0	11.1	2.5
4	Diflufenican	18.31	9.7	8.7	10.6	9.9	9.3	9.7	7.3
5	Fenamiphos	16.24	8.9	8.2	9.4	9.0	9.4	9.0	5.6
6	Fenarimol	20.20	10.2	10.2	10.1	10.5	10.4	10.3	1.6
7	Fenpropiomorph	14.74	10.9	11.0	11.1	11.8	10.8	11.1	3.5
8	Norflurazon	17.94	9.5	9.5	9.5	10.2	10.0	9.7	3.3
9	Oxadiazon	16.50	9.5	9.2	10.4	9.6	9.8	9.7	4.8
10	Penconazole	15.45	10.8	10.6	11.0	11.0	10.8	10.8	1.6
11	Pendimethalin	15.29	11.5	11.4	11.3	11.4	13.1	11.7	6.7
12	Procyimidone	15.70	10.9	10.5	9.1	12.1	9.7	10.5	10.7
13	Spiroxamine1	13.78	9.7	9.9	10.2	10.8	10.5	10.2	4.3
14	Spiroxamine2	14.31	10.0	9.3	10.2	10.1	10.2	10.0	4.0
15	Tefluthrin	12.92	10.6	10.1	10.8	11.6	10.5	10.7	5.4
16	Terbufos	12.63	8.3	8.0	8.7	9.2	8.4	8.5	5.3
17	Terbutryn	14.31	10.0	9.7	10.5	10.4	10.4	10.2	3.6
18	trans-Permethrin	20.68	11.0	10.8	11.5	11.2	11.0	11.1	2.5
19	Alachlor	13.84	9.1	9.0	9.9	10.1	9.3	9.5	5.2
20	Buprofezin	16.68	12.0	9.8	10.5	11.5	11.8	11.1	8.5
21	cis-Chlorfenvinphos	15.49	8.2	7.8	9.1	8.8	8.8	8.6	5.9
22	Cyproconazole 1	17.03	9.3	10.0	10.8	9.8	8.4	9.7	9.1
23	Cyproconazole 2	17.03	11.3	10.2	10.2	11.8	12.6	11.2	9.3
24	Difenoconazole 1	23.10	10.5	10.4	10.5	10.5	10.4	10.5	0.7
25	Difenoconazole 2	23.18	10.6	10.5	10.5	10.6	10.6	10.6	0.5
26	Ethion	17.34	9.1	8.4	9.7	8.9	8.7	9.0	5.6
27	Fenitrothion	14.33	7.9	6.9	7.3	7.4	6.6	7.2	7.2
28	Fenthion	14.73	9.3	7.9	8.5	9.1	8.2	8.6	7.2
29	Fluridone	22.18	11.2	11.4	11.5	11.5	10.1	11.2	5.5
30	Hexazinone	18.24	8.3	8.0	9.1	8.9	8.8	8.6	4.8
31	Isofenphos oxon	14.79	9.3	9.3	10.1	10.4	9.2	9.7	5.6
32	Isophenphos	15.43	9.8	9.6	10.3	9.5	9.9	9.8	3.0
33	Isoprothiolane	16.44	10.2	9.9	10.9	10.2	9.6	10.2	4.4
34	Propargite 1	18.31	7.7	7.4	8.8	8.1	8.1	8.0	6.8
35	Propargite 2	18.31	8.4	7.8	9.1	8.7	8.4	8.5	6.0
36	Propiconazole 1	17.93	11.5	10.4	10.8	11.5	10.8	11.0	4.5
37	Propiconazole 2	18.07	11.8	11.3	11.2	11.1	10.7	11.2	3.5
38	Propyzamide	12.73	10.6	9.8	10.6	10.9	10.5	10.5	3.9
39	Pyriproxyfen	19.72	10.0	10.4	10.7	10.4	9.7	10.2	3.8
40	trans-Chlorfenvinphos	15.25	10.6	9.5	10.2	10.6	10.5	10.3	4.3
41	Triadimenol 1	15.70	10.2	7.7	9.6	9.9	8.7	9.2	11.1
42	Triadimenol 2	15.84	10.7	9.4	9.9	10.3	9.8	10.0	4.7
43	Triallate	13.13	7.5	7.3	7.6	8.1	7.6	7.6	3.5
44	Vinclozoline	13.76	8.1	8.2	8.1	9.2	8.6	8.4	5.6
45	Acetamidrid	18.92	10.8	8.7	9.6	9.3	10.3	9.7	8.6
46	Allethrin 1	15.43	12.0	9.6	11.6	11.1	11.8	11.2	8.5
47	Allethrin 2	15.51	6.4	6.6	7.3	7.5	7.3	7.0	7.1
48	Bitertanol 1	20.66	12.1	12.1	12.5	12.3	12.2	12.3	1.2
49	Bitertanol 2	20.76	9.6	9.6	10.3	10.0	10.0	9.9	3.1
50	Bromopropylate	19.00	8.7	8.3	9.1	9.3	9.2	8.9	4.4
51	Chlorobenzilate	17.19	7.8	7.0	8.2	7.9	7.6	7.7	5.5
52	Chlorpyrifos	14.63	8.5	8.2	8.9	9.9	9.9	9.1	8.6
53	Oxyfluorfen	16.59	11.6	11.1	9.1	9.5	11.2	10.5	10.7
54	Parathion	14.80	9.1	8.8	7.5	7.8	8.7	8.4	8.0
55	Pirimiphos methyl	14.24	9.3	9.2	9.6	10.0	9.7	9.6	3.5
56	Propanil	13.67	9.8	9.2	9.8	10.0	10.6	9.9	5.0
57	Pyridaben	20.87	10.4	9.8	10.9	10.5	9.9	10.3	4.5
58	Quinoxifin	18.00	11.2	10.7	11.4	11.5	11.0	11.2	2.8
59	Simazine	12.29	9.3	9.8	9.7	9.8	8.7	9.5	4.9
60	Tebuconazole	18.38	10.8	10.2	9.4	10.9	10.1	10.3	5.9
61	Triadimefon	14.87	10.4	12.5	11.5	11.1	11.0	11.3	7.0
62	Triazophos	17.65	7.7	7.3	7.6	7.2	7.0	7.3	3.7
63	Ametryn	14.00	9.7	9.9	10.2	9.9	9.8	9.9	1.6
64	Azaconazole	16.83	12.4	12.4	12.8	13.3	12.8	12.7	3.1
65	Bupirimate	16.66	10.5	10.6	11.1	11.5	11.8	11.1	5.0
66	Butachlor	16.01	9.5	9.4	9.7	9.6	9.9	9.6	1.8
67	Chlorthal dimethyl	14.73	9.0	8.5	9.3	9.0	9.6	9.1	4.6
68	Dicloran	12.19	8.0	7.7	9.2	8.7	8.4	8.4	7.3
69	Diethofencarb	14.63	10.6	10.5	11.1	10.7	10.6	10.7	2.2
70	Dimepiperate	15.74	12.0	12.2	13.3	11.3	11.7	12.1	6.2
71	Dimethenamid	13.61	10.9	10.9	11.2	11.1	10.8	11.0	1.4
72	Etiozazole	19.03	10.7	9.2	10.8	10.6	9.5	10.2	7.3
73	Fluacrypyrim	17.38	9.8	9.6	10.2	10.3	10.5	10.1	3.7
74	Lenacin	18.14	11.4	11.4	11.5	11.3	11.5	11.4	0.6
75	Pyriminobac methyl 1	17.96	12.3	12.0	11.4	11.8	12.0	11.9	2.7

No.	Compound	RT (min)	Quantitative value (ppb)					Ave. (ppb)	CV (%)
			No.1	No.2	No.3	No.4	No.5		
76	Pyriminobac methyl 2	12.88	10.6	10.5	10.0	11.0	10.6	10.5	3.5
77	Pyroquilon	19.53	9.6	10.2	10.0	10.9	9.8	10.1	4.8
78	Tetradifon	13.87	7.1	7.3	8.6	8.4	7.8	7.8	8.1
79	Tolclofos-methyl	16.61	9.7	8.8	10.3	9.7	10.2	9.7	5.8
80	Uniconazole P	13.66	9.7	9.9	10.5	10.5	10.1	10.2	3.7
81	Acetochlor	17.83	9.5	11.7	12.1	11.9	10.3	11.1	10.3
82	Benalaxyl	13.57	9.2	9.2	10.4	9.4	8.5	9.3	7.3
83	Benfuresate	11.71	10.2	9.1	9.9	9.8	9.3	9.6	4.6
84	Cadusafos	11.37	8.1	9.0	8.9	9.4	8.9	8.9	5.7
85	Chlorpropham	15.61	9.2	8.7	8.9	9.4	9.0	9.0	3.1
86	Diclocymet 1	15.91	10.3	10.6	10.5	10.6	9.7	10.3	3.6
87	Diclocymet 2	15.40	10.0	9.4	9.3	10.2	9.8	9.7	3.7
88	Dimethametryn	14.49	11.3	11.4	11.5	11.2	10.9	11.3	2.0
89	Esprocarb	21.83	9.2	9.3	9.8	9.3	8.9	9.3	3.3
90	Etofenprox	16.08	11.5	11.8	11.7	11.5	11.5	11.6	1.0
91	Fenothiocarb	13.27	10.7	10.2	10.3	10.3	10.5	10.4	1.8
92	Iprobenfos	16.92	9.2	9.3	9.8	9.8	9.6	9.5	2.6
93	Isoxathion	17.61	6.9	6.0	7.5	7.4	7.0	7.0	8.4
94	Mepronil	14.04	10.7	10.2	10.3	10.0	10.4	10.3	2.5
95	Prometryn	10.85	10.1	9.6	10.3	10.4	9.7	10.0	3.6
96	Propachlor	16.41	9.6	8.6	9.1	9.9	9.2	9.3	5.4
97	Prothiofos	15.99	8.4	9.0	9.1	9.3	7.4	8.6	8.7
98	Pyrifenoxy 1	12.89	10.9	10.2	10.1	9.8	9.1	10.0	6.5
99	Pyrimethanil	13.94	9.6	10.1	9.8	9.9	9.1	9.7	3.9
100	Simetryn	13.06	10.8	10.0	11.3	10.8	10.3	10.6	4.9
101	Terbacil	14.82	12.4	12.6	13.3	12.5	13.1	12.8	3.0
102	Tetraconazole	18.31	12.0	12.6	11.3	12.3	10.8	11.8	6.3
103	Thenylchlor	16.58	7.7	8.3	8.8	8.4	8.2	8.3	4.9
104	Tribufos	16.66	8.8	8.4	8.7	9.0	9.1	8.8	2.9
105	Tricyclazole	15.72	7.5	6.9	9.4	9.0	8.4	8.2	12.3
106	Zoxamide (decomposed)	13.40	10.2	9.8	10.5	9.5	10.2	10.0	3.7
107	Benoxacor	14.44	8.1	7.9	8.5	7.9	7.4	8.0	4.8
108	Bromacil	13.70	9.3	7.3	10.1	8.6	8.7	8.8	11.4
109	Bromobutide	16.17	11.2	15.3	14.0	12.5	12.6	13.1	11.9
110	Butamifos	13.56	10.1	10.0	11.0	10.5	10.1	10.3	4.1
111	Dichlorfenthion	15.12	10.1	10.0	10.2	10.5	9.8	10.1	2.6
112	Diphenamid	16.42	12.3	11.6	11.9	12.1	11.6	11.9	2.7
113	Hexaconazole	14.00	10.3	10.3	10.5	10.3	10.4	10.4	1.0
114	Mefenoxam	16.33	9.3	10.2	10.0	9.3	9.8	9.7	4.3
115	Napropamide	17.40	10.1	9.6	9.4	10.3	10.1	9.9	3.7
116	Oxadixyl	16.07	10.5	10.3	10.5	10.5	10.2	10.4	1.3
117	Paclobutrazol	19.31	11.5	10.7	10.9	10.6	11.3	11.0	3.5
118	Phenothrin 1	19.42	11.3	12.7	12.6	11.9	12.9	12.2	5.5
119	Phenothrin 2	18.98	10.2	10.4	10.7	10.7	10.5	10.5	2.0
120	Piperophos	12.94	9.1	9.2	9.5	10.2	9.2	9.4	4.9
121	Prohydrojasmon 1	13.23	8.6	8.2	8.9	9.3	8.9	8.8	4.8
122	Prohydrojasmon 2	12.42	12.7	9.9	10.5	8.5	9.2	10.2	15.7
123	Propazine	18.63	10.1	10.2	10.2	10.0	9.7	10.0	2.0
124	Pyributicarb	15.51	12.1	11.5	11.7	11.9	11.8	11.8	1.9
125	Pyrifenoxy 2	15.63	10.4	9.9	9.8	10.1	9.6	10.0	3.1
126	Quinalphos	19.16	10.5	10.0	10.7	10.6	10.0	10.3	3.4
127	Tebufenpyrad	24.05	9.0	9.8	10.0	9.8	9.3	9.6	4.1
128	Tolfenpyrad	14.78	9.3	9.6	9.4	9.7	9.3	9.5	1.7
129	Aldrin	16.26	7.6	7.6	7.4	8.0	7.5	7.6	3.2